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Laser diagnostics of reverse microemulsions in the process of nanoparticle synthesis

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In this work, laser spectroscopy was used to study reverse microemulsions, in which the reaction of ZnS nanoparticle synthesis was carried out. The sizes of the synthesized nanoparticles do not exceed 5 nm. As a result of studying the processes in the reaction medium, it was found that the band of stretching vibrations of HS^- ions in the region of $2568\,cm^{-1}$ is an identification sign of the synthesis of nanoparticles: by its intensity it is possible to determine the stage and completion of the ZnS synthesis.

Keywords: nanoparticle synthesis, nanoreactors, laser diagnostics, Raman spectroscopy, reverse microemulsions.

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The active use of nanomaterials in medicine, energy, ecology and other areas of science and industry requires nanoparticles of various sizes and shapes [1]. That is why today various methods for the synthesis of nanoparticles are being intensively developed. Among the many existing methods, synthesis in reverse microemulsions can be highlighted, which allows to obtain nanoparticles with a narrow size distribution. The parameters of the reaction medium (temperature, concentration of substances) and the parameters of the experimental setup are usually varied in most methods for obtaining nanoparticles of certain shapes and sizes. The results can only be judged after stopping the synthesis, multi-stage purification processes of nanoparticles, and characterization of nanoparticles by various methods. Despite the development of various synthesis methods and methods for continuous monitoring of processes occurring in the reaction medium, there are practically no express methods for determining the parameters of nanoparticles. Thus, the development of a method for remote control of the sizes of synthesized nanoparticles in real time is a very urgent task. Laser Raman scattering (RS) spectroscopy of light is a remote and very informative method that allows to study in real time the properties and interactions of solution components [2], and also provides a successful quantitative solution to inverse problems of laser spectroscopy [2,3], in particular, determination of the sizes of reverse micelles in microemulsions [3].

The synthesis of semiconductor nanoparticles is of great interest to researchers due to their special physical properties and wide application in various fields of science and industry [4]. Zinc sulfide nanoparticles ZnS are often used to oxidize organic matter in wastewater treatment due to their photocatalytic properties [5], they are nanoscale „building“ blocks in biosensors [6], are used to create a supercapacitor electrode [7], and the authors [8] demonstrated the antibacterial effectiveness of these nanoparticles.

In this work, using RS spectroscopy, dynamic light scattering (DLS), and absorption spectroscopy in the ultraviolet region, the processes in micellar nanoreactors with ZnS nanoparticles synthesized in them were studied.

To prepare reverse microemulsions, sodium bis(2-ethylhexyl)sulfosuccinate (AOT, 99.6 mas%), n-heptane (99.9 mas%), ultrapure deionized water were used. $ZnSO_4 \cdot 7H_2O$ (99.8 mas%) and $Na_2S \cdot 9H_2O$ (97.7 mas%) acted as precursors of ZnS nanoparticles. A solution of AOT in heptane with a concentration of 0.15 mol/kg and a 2 aqueous solution of each of the salts $ZnSO_4$ and Na_2S with concentrations of 0.2 mol/kg were obtained to prepare microemulsions.

Both microemulsions were prepared by mixing aqueous solutions of each salt with an AOT/heptane solution so that the $w = [\text{water}]/[\text{AOT}]$ parameter for all the resulting microemulsions was the same and equal to 4.

The synthesis of ZnS nanoparticles was carried out by mixing equal volumes of two microemulsions containing equal amounts of Zn^{2+} and S^{2-} ions, and subsequent stirring of the resulting reaction medium for 5 min.

A laser RS spectrometer was used to obtain RS spectra of microemulsions. The RS signal was excited by a diode pumping solid-state laser ($Q_{exc} = 532$ nm, power 800 mW). The 90° experiment geometry was used.

The spectra recording system consisted of an Acton 2500i monochromator and a Jobin Yvon CCD camera (Syncerity model). A RapidEdge RPE540LP filter (Omega Optical) was used to suppress elastic scattering at the excitation wavelength (532 nm). The practical resolution

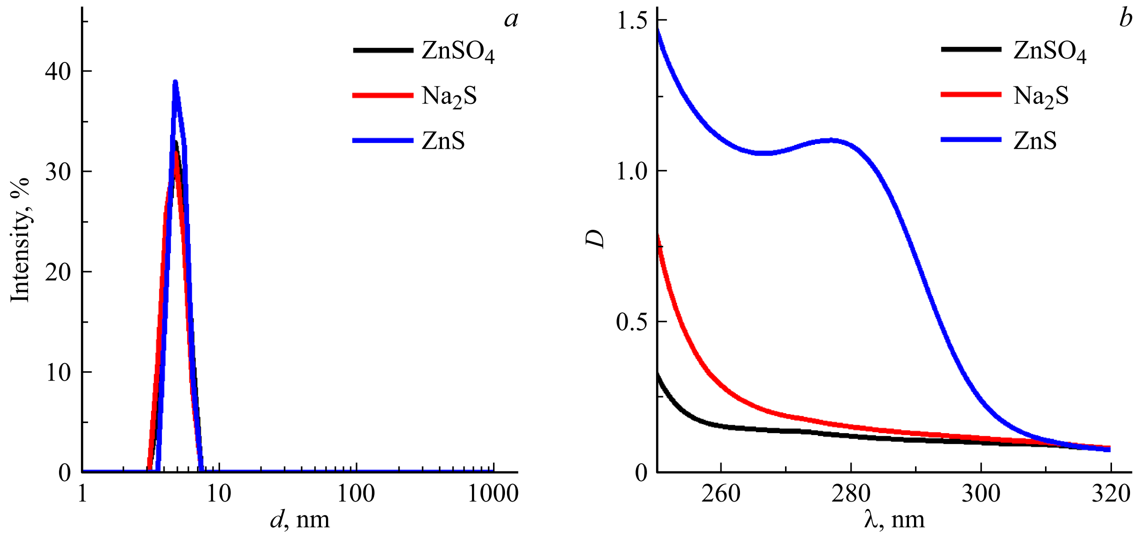

Figure 1. Distributions of scattering intensity on hydrodynamic diameters d of reverse micelles (a) and dependence of absorbance$D$ on wavelength λ (b) for three microemulsions containing $ZnSO_4$, Na_2S and ZnS nanoparticles, correspondingly.

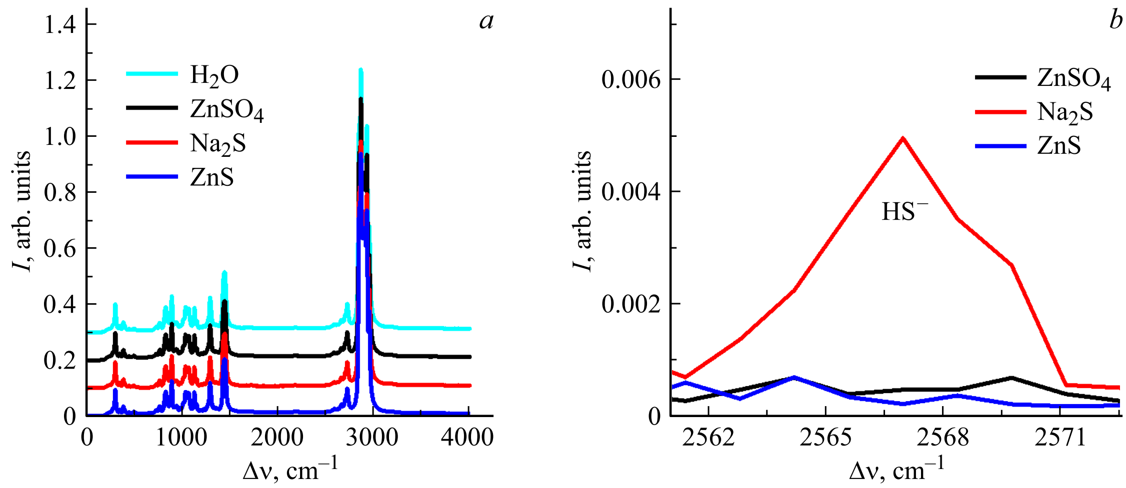

Figure 2. RS spectra of the studied microemulsions (a) (for clarity, each spectrum is shifted upward by 0.1 in intensity relative to the bottom). Difference spectra of microemulsions containing $ZnSO_4$, Na_2S ZnS (b).

in the region of the water valence band was $1.5\,cm^{-1}$. The RS spectrum recording time was 20 s. Determination of the sizes of synthesized nanoparticles and reverse micelles was carried out on a Malvern ZetaSizer Nano ZS ($\lambda = 632.8$ nm) device. To obtain absorption spectra in the ultraviolet region (250–320 nm) of microemulsions, a Shimadzu U-1800 spectrophotometer was used.

Using the DLS method, the hydrodynamic sizes of reverse micelles of three microemulsions containing aqueous solutions of $ZnSO_4$, Na_2S and synthesized ZnS nanoparticles were determined, respectively: distributions of scattering intensity from particle sizes in microemulsions were obtained (Fig. 1, a). As follows from the DLS data (Fig. 1, a), the reverse micelles in all three microemulsions have the same dimensions 5.0 ± 0.8 nm. The DLS results show that the nanoparticles that could be formed during the synthesis do not exceed the size of micelles (Fig. 1, a).

For all the studied microemulsions, absorption spectra were obtained in the ultraviolet region in the range from 250 to 320 nm (Fig. 1, b). As can be seen from Fig. 1, b, microemulsions in which zinc sulfide nanoparticles were synthesized have an absorption band in the region of 280 nm that is absent in the original salt solutions (i.e., ions Zn^{2+}, SO_4^{2-}, Na^+, S^{2-}, into which salts dissociate in water, there is no absorption in this region). Since as a result of the synthesis of ZnS nanoparticles, only SO ions ${}_4^{2-}$ and Na^+ remain in the aqueous solution, the appearance of an absorption band in the region of 280 nm indicates the formation of ZnS nanoparticles.

RS spectra were obtained for four AOT microemulsions with reverse micelles containing in their cores water, an aqueous solution of ZnSO4 (0.2 mol/kg), an aqueous solution of Na_2S (0.2 mol/kg) and an aqueous suspension of synthesized ZnS nanoparticles, respectively (Fig. 2, *a*). In the RS spectrum of microemulsions, the most intense bands are due to vibrations of heptane and AOT groups: stretching vibrations of CH in the region of $2800-3050\,cm^{-1}$, bending vibrations of CH_2 and CH_3 groups in the region of $1100-1500\,cm^{-1}$ (Fig. 2, *a*). The stretching band of water in the region of $3000-3700\,cm^{-1}$, the deformation band of water in the region of $1640\,cm^{-1}$, the valence band of SO_4^{2-}groups in the region with a maximum of $980\,cm^{-1}$ against the background of the heptane and AOT lines on the scale shown in Fig. 2, *a* cannot be seen. To analyze the state of the components of the reaction medium located in the cores of reverse micelles, difference spectra were obtained: from the spectra of microemulsions with salt solutions and ZnS nanoparticles, the spectrum of a microemulsion with water in the core of micelles was subtracted (Fig. 2, *b*).

As can be seen from Fig. 2, *b*, in the difference spectrum of a microemulsion containing Na_2S salt, there is a band with a maximum I$2567.5 \pm 1.5\,cm^{-1}$, which corresponds to the stretching vibrations of the HS^- ions formed in an aqueous solution as a result hydrolysis of Na_2S [9]. In microemulsions where the synthesis of ZnS nanoparticles occurred, the band of stretching vibrations of the HS^- ions is absent (Fig. 2, *b*). This band is also absent in microemulsions with $ZnSO_4$ (Fig. 2, *b*). This behavior of the HS band is likely due to a decrease in free S^{2-} ions in the reaction medium as a result of the combination of these ions with Zn^{2+} ions as ZnS nanocrystals form and grow. Thus, the intensity of the HS^- valence band can be used to judge the intermediate stage and completion of the nanoparticle synthesis process.

In this work, microemulsions in which the synthesis reaction of ZnS nanoparticles was carried out were studied using RS spectroscopy, ultraviolet absorption spectroscopy and dynamic light scattering. The results obtained allow to develop a non-contact and rapid method for diagnosing the reaction medium during the synthesis of nanoparticles in them.

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Conflict of interest

The authors declare that they have no conflict of interest.

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