

# Preparation of Composite of ZnS Nanoparticles and Montmorillonite by Cavitation Deposition

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## ABSTRACT

Physics and chemistry of very small particles emanate from a long-term tradition of colloidal chemistry. An important area of contemporary nanotechnologies is preparation of nanoparticles with size lower than 100 nm by top-down and bottom-up methods. Bottom-up methods turned out to be more suitable for preparation of nanoparticles than methods based of various chemical reactions. In our previous works we referred about preparation of ZnS nanoparticles with size about 3-5 nm stabilized by cationic surfactants like cetyltrimethylammonium bromide (CTAB) in aqueous dispersions by chemical precipitation of zinc acetate and sodium sulphide. CTAB was found to significantly influence size of ZnS nanoparticles. A basic requirement for their photocatalytic properties is maximal reactive surface area. For practical manipulation these nanoparticles were deposited on caring larger particles which formed dry powders. In this work, a new method for preparation of composite of ZnS nanoparticles and montmorillonite ZnS-MMT in aqueous environment is presented. The ZnS-MMT nanocomposite was formed by cavitation implosion of ZnS nanoparticles into MMT pores. As a result of very high impact velocities at collisions of ZnS nanoparticles and MMT particles increase of a number of ZnS nanoparticles in ZnS-MMT can be expected. The method of cavitation deposition utilizes implosion of cavitation bubbles, which were formed by nucleation on external surface of dispersed particles. Extreme dynamics of implosion collapse of cavitation bubbles leads to formation of high impact pressures up to tents GPa in final implosion phase. Density of nanoparticles in the aqueous dispersion is very high and cavitation bubbles nucleated on walls of the caring MMT particles catch photoactive ZnS nanoparticles on expanding surface with high probability. At the end of tensile stress in liquid a bubble implosion collapse as well as a collision between both particles happen. The deposition happens with high frequency and energy. Performed analyses showed that the method of cavitation deposition

lead to increase of specific surface area at cca 214 % of that originated by standard mechanical shaking. The total content of ZnS in the ZnS-MMT composite increased from 7 wt. % (shaking) to 10.5 wt. %. If ZnS nanoparticles are bound to surface of a caring material in a monolayer arrangement then nanocomposite photocatalytic efficiency should be proportional to product of specific surface area and a total content of deposited ZnS. Hence, the photocatalytic efficiency of ZnS-MMT nanocomposite prepared by the cavitation method was about 300 % in comparison with the composite prepared by shaking.

**Keywords:** nanoparticle, ZnS, photocatalytic, cavitation, montmorillonite, vacuum freeze-drying

## 1 INTRODUCTION

Our previous works in the field of nanoparticles [1-3] were focused on research about preparation and properties of ZnS nanoparticles ( $d \approx 3-5$  nm) synthesized by precipitation reaction of sodium sulfide and zinc acetate in aqueous solutions with surfactant cetyltrimethylammonium bromide (CTAB). It limited the size of the precipitated nanoparticles and stabilized their dispersion in the liquid medium. Due to the semiconducting properties the zinc sulfide can be used in photocatalytic applications and degradation of undesirable substances [4]. The efficiency of photocatalytic materials is naturally proportional to the size of the interfacial interface. In this respect nanoparticles provide very favorable ratio of the volume consumption of the active material (in our case ZnS) per unit area of the outer surface. The synthesized nanoparticles ZnS represent in the resulting aqueous dispersion only very small volume fraction and for better practical handling in the dry state it is necessary to deposit them on the surface of larger carrier particles with which they may create a macroscopic dry powder.

To achieve the above effect, 300 ml of aqueous dispersion of ZnS nanoparticles was sterically stabilized by creating micellar shell from  $\text{CTA}^+$  ions around ZnS nanoparticles. This dispersion was shaken together with microparticles of montmorillonite MMT ( $d < 5 \mu\text{m}$ ) for 24

hours. [2]. ZnS nanoparticles were deposited on the surface and into pores of larger carrier particles of montmorillonite MMT by simultaneous action of electrostatic forces, the zeta-potential and Van der Waals forces. Nanocomposite aggregates of ZnS-MMT were then centrifuged and captured on the filter paper. The filter cake was washed several times with demineralised water and then dried in a heating oven at 70 °C and comminuted to form a micropowder for convenient manipulation in photocatalytic applications in dry environments.

## 2 A METHOD OF CAVITATION DEPOSITION OF NANOPARTICLES TO LARGER CARRIER MICROPARTICLES

In this work we present preliminary results and analysis of the practical application of a new method of cavitation deposition of photoactive ZnS nanoparticles into the supporting composite microparticles ZnS-MMT in aqueous dispersion. In artificially induced conditions of intense microcavitation in mixed aqueous dispersion of ZnS nanoparticles and microparticles montmorillonite MMT is preferred heterogeneous nucleation of cavitation bubbles on the surface of these particles. The cavitation deposition method utilizes the implosion of the cavitation bubbles. Extreme dynamics of implosive collapse of cavitation bubbles themselves were described in [5]. The collapse of pure steam cavitation bubbles leads to high impact pressures up to tens of GPa in the final stage of implosion.

The volume concentration of ZnS nanoparticles in aqueous dispersion is high and almost every cavitation bubble, which is nucleated on the wall of microparticles MMT, is captured with a significant probability by its expanding interface of any ZnS nanoparticle. Termination of tensile stresses in the liquid leads to instability of cavitation and implosive collapse of bubbles between both particles as schematically is shown in Figure 1.

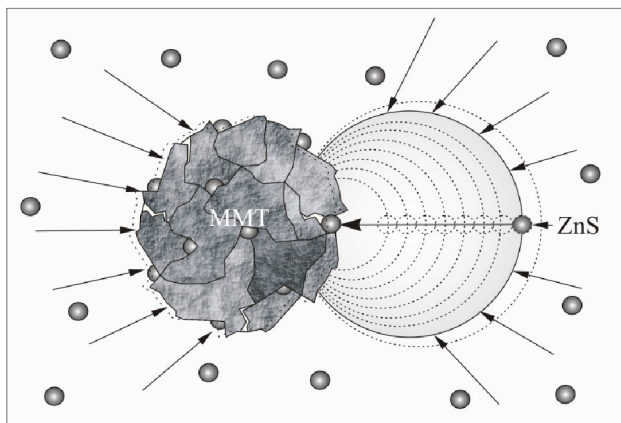


Figure 1: Cavitation implosion of the bubble and high energy impact of bubble interface comoving ZnS nanoparticles on external surface of MMT

Due to considerably higher impact speed of ZnS on the MMT surface and higher frequency of collisions, increased number of nanoparticles in the final nanocomposite ZnS can be expected. In a practical realization of cavitation deposition, as first MMT particles were disintegrated during intensive turbulent mixing in the ultrasonic field of 50 W/L for 30 min in an aqueous fine microdisperse and then dried by vacuum freeze at -24 °C. The dried product with an increased specific surface area was added into the aqueous dispersion of ZnS nanoparticles. Then it was subjected for 30 min to an intensive turbulent mixing in the ultrasonic field. The dispersion was transferred to a dry nanocomposite powder ZnS-MMT by vacuum sublimation at -24 °C.

## 3 EXPERIMENTAL

For subsequent comparison efficiency of cavitation deposition, in the first phase ZnS-CTA nanoparticles were prepared by precipitation reaction, then deposited on the MMT microparticles by shaking MMT with ZnS-CTA for 24 hours [2]. Thus standard nanocomposite was prepared as shown in Figure 2.

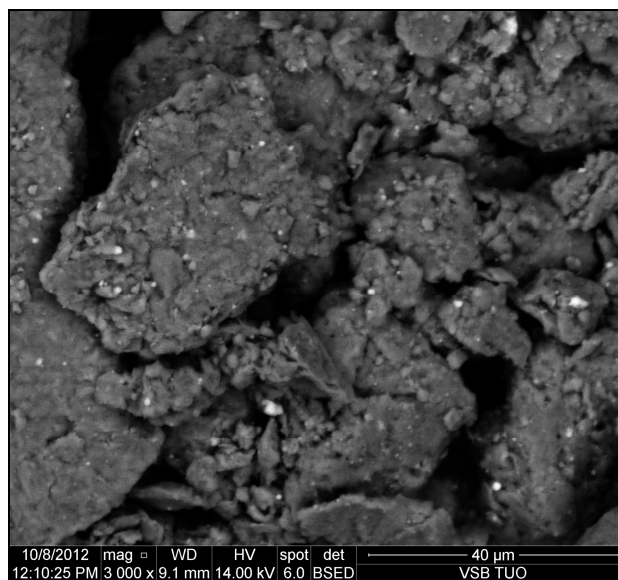


Figure 2: The SEM micrographs of dry powder nanocomposite of microparticles ZnS- MMT prepared by shaking method

In Figure 2 is shown a relatively compact aggregate structure of dried standard material.

New nanocomposite material prepared by deposition of cavitation (see Figure 3) reveals distinct lamellar structure with a significantly lower level of aggregation.

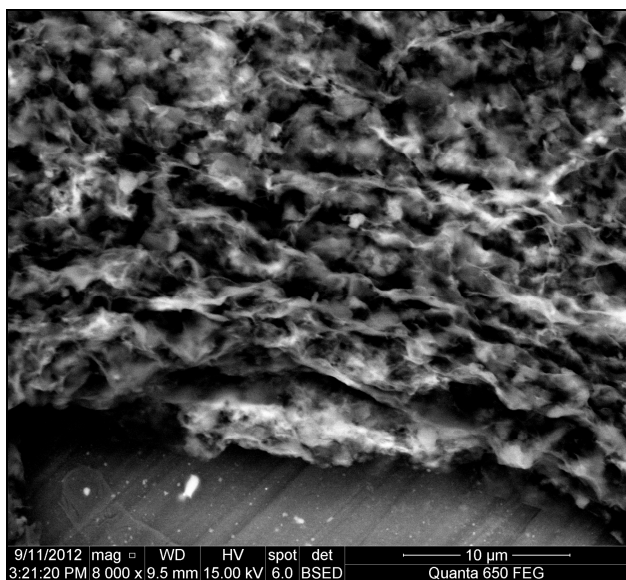


Figure 3: The SEM micrographs of dry powder nanocomposite of microparticles ZnS-MMT prepared by cavitation deposition

To compare the efficiency of deposition of both methods energy dispersive X-ray spectroscopic microanalysis EDAX of six different surface areas of 100x100 micron on each type of material was also carried out. In the depth of penetration about 5 μm by excited electrons, the microanalysis reveals about 1.5 times higher content of ZnS nanoparticles deposited by cavitation method than in case of deposition by shaking for 24 hours. For further photocatalytic applications, a high content of accessible ZnS semiconductor nanoparticles disposed on the maximum surface of MMT microparticles is required. specific surface area (SSA) and also cumulative pore volume  $V_{\text{pore}}$  of ZnS-MMT nanocomposites prepared by both methods were measured by BET isotherm method.

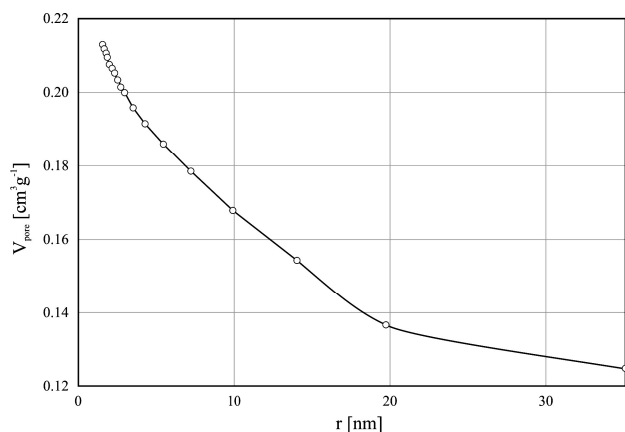


Figure 4: Porosimetric analysis of nanocomposite photocatalytic material ZnS-MMT prepared by shaking

Dry nanocomposite material prepared by the standard shaking method showed  $SSA = 37,2 \text{ m}^2 \text{ g}^{-1}$  and  $V_{\text{pore}} = 0,214 \text{ cm}^3 \text{ g}^{-1}$  (see Figure 4), while the new material prepared by cavitation deposition showed more than twice the magnitude of  $SSA = 79,5 \text{ m}^2 \text{ g}^{-1}$  and  $V_{\text{pore}} = 0,983 \text{ cm}^3 \text{ g}^{-1}$  (see Figure 5).

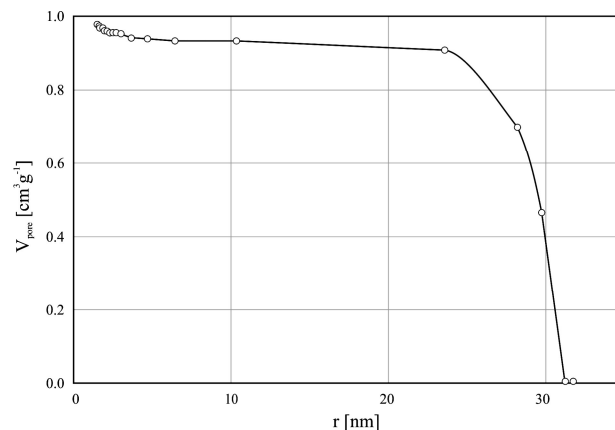


Figure 5: Porosimetric analysis of nanocomposite photocatalytic material ZnS-MMT prepared by cavitation deposition

Current preliminary measurements show that the method of cavitation deposition leads to an increase in surface area approximately to 214 % of the standard value after the application of methods of shaking. Also, the total content of about 7 wt. % zinc sulfide in standard composite ZnS-MMT prepared by shaking [2] was in the alternative preparation by cavitation deposition increased to 150 % of the original content (10.5 wt. %).

## CONCLUSIONS AND FUTURE DIRECTIONS

Preliminary experimental experiences with cavitation deposition of ZnS nanoparticles creating nanocomposite carrier ZnS-MMT particles confirmed the basic assumptions of the theoretical model resulting from the implosion of cavitation bubbles between two particles. Measurement of parameters of the resulting nanocomposite material ZnS-MMT after cavitation deposition confirms the expected increase in the density of ZnS nanoparticles which were deposited on the surface at its present more than two-fold increase. Assuming that ZnS nanoparticles are bound on the surface of carrier particles in a single layer, the photocatalytic activity should be proportional to the product of specific surface area and total content of deposited ZnS with respect to the morphology of the nanocomposite material. In this extreme situation, cavitation deposited material ZnS-MMT shows in comparison with standard material increase of the photocatalytic efficiency up to 300 % of the original value.

## ACKNOWLEDGMENTS

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