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Office of Naval Research
Contract N00014-87-K-0738
Task No. 431a020
Technical Report No. 4

PREPARATION AND CHARACTERIZATION OF COLLOIDAL ZnS PARTICLES

by

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Prepared for Publication

in the

Materials Research Society Symposium on
Science of Colloidal Processing

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June 15, 1989

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release Distribution unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) #4			5. MONITORING ORGANIZATION REPORT NUMBER(S) N00014-87-K-0738		
6a. NAME OF PERFORMING ORGANIZATION Iowa State University Mufit Akinc		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Dr. R. Schwartz	
6c. ADDRESS (City, State, and ZIP Code) 110 Engineering Annex Materials Science & Engineering Dept. Ames, IA 50011			7b. ADDRESS (City, State, and ZIP Code) Code 38504 Naval Weapons Center China Lake, CA 93555-6001		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT NO. 4312020
11. TITLE (Include Security Classification) Preparation and Characterization of Colloidal ZnS Particles					
12. PERSONAL AUTHOR(S) Ahmet Celikkaya and Mufit Akinc					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 89/06/15	
15. PAGE COUNT 6					
16. SUPPLEMENTARY NOTATION Submitted to Materials Research Society					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED, UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS					
22a. NAME OF RESPONSIBLE INDIVIDUAL			21. ABSTRACT SECURITY CLASSIFICATION		22b. TELEPHONE (Include Area Code)
					22c. OFFICE SYMBOL

PREPARATION AND CHARACTERIZATION OF COLLOIDAL ZnS PARTICLES

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INTRODUCTION

The preparation of particles of uniform size, shape, and composition has been of interest to colloid chemists and has received serious attention in the ceramic processing community recently. The interest in making monodispersed sols is not based solely on esthetic appeal of such systems but has evolved from high tech applications which place stringent requirements on the properties of ceramic components and so on starting powders. Uniform particle size and shape are also essential for the evaluation of validity of various sintering models as well as optical, magnetic and electrokinetic properties of colloidal systems developed assuming uniform particle size and shape. *JES*

ZnS powders has long been prepared by various methods including gas phase, solid/vapor and aqueous solution reactions [1-5]. Chiu [3] was the first to prepare monodisperse ZnS sols by passing H_2S into Zn^{2+} solutions in the presence of EDTA. The particles were $0.2 \mu m$ in diameter but the solutions were too dilute to be of any practical value. Later, Wilhelmy and Matijevic [4] employed thermal decomposition of thioacetamide to prepare micron-sized spherical particles by aging the reaction mixture several hours. Williams et. al. [5] employed the same technique to prepare monosized, spherical particles of ZnS about $3 \mu m$ in diameter. However, a review of the latter two works indicates that subtle variations in experimental procedures not only the particle size but also mechanism of particle growth, crystalline phases produced and particle morphology.

In this article, the role of various anions in the kinetics of precipitation and the morphology of the particles will briefly be discussed.

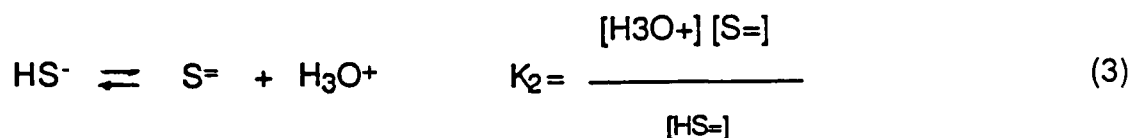
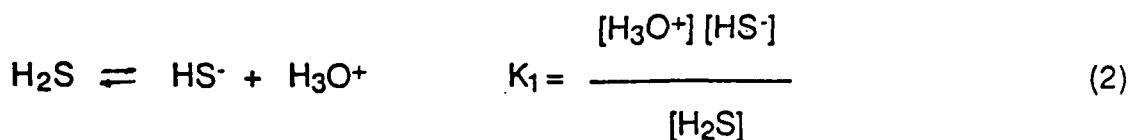
RESULTS AND DISCUSSION

ZnS powders were prepared by thermal decomposition of thioacetamide in acidic zinc solutions ($pH \leq 2$). Process involves decomposition of thioacetamide according to the reaction

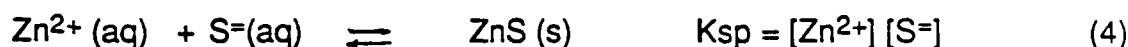


and dissociation of hydrogen sulfide in two steps producing sulfide ions

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which cause precipitation of ZnS when the critical supersaturation is reached. The equilibrium precipitation reaction is given by



Slow introduction of sulfide ions into the system forms the basis for producing uniform particles. Rate of sulfide ion generation is determined by decomposition of thioacetamide and can be controlled by appropriate choice of experimental parameters such as, temperature, pH, and the initial concentration of thioacetamide. It was found that the critical supersaturation defined as

$$S = \left(\frac{[\text{S}^{2-}]_t [\text{Zn}^{2+}]}{K_{\text{sp}}} \right)^{1/2}$$

where $[\text{S}^{2-}]_t$ is sulfide ion concentration at any time t , and K_{sp} is the solubility product for β -ZnS remains constant at a value of about 10 for any combination of experimental variables [6]. Zinc ion concentration $[\text{Zn}^{2+}]$ was kept constant at 0.05 M so that the time elapsed to nucleation represents a relative measure of sulfide ion generation rate.

Figure 1 shows electron micrographs of particles precipitated under various conditions in the presence of nitrate ions (i.e. zinc nitrate stock solutions were used as Zn^{2+} source and pH of the solutions were adjusted with HNO_3). Reaction mixtures were aged for 1 hour. Observed variation of the type of the particle size distribution is related to the difference between rates of sulfide ion generation and its consumption in the growth process. Monosized particles were obtained at low rates of sulfide ion generation (Figure 1a). At intermediate sulfide ion generation rates, a net buildup of excess sulfide ions leads to formation of a second burst of nuclei, resulting in a bimodal distribution (Figure 1b). If sulfide ions are not consumed at a high enough rate even after formation of second generation of particles, a third, fourth etc., nucleation events are expected resulting in a continuous distribution of particle sizes (Figure 1c).



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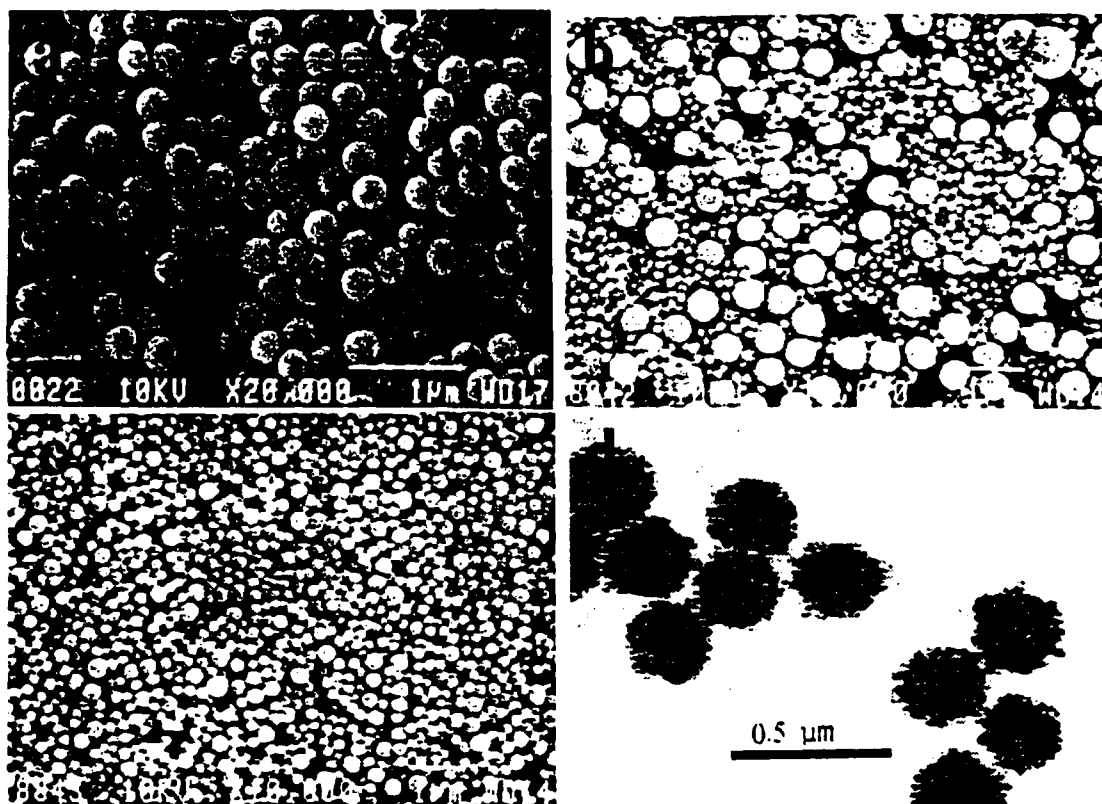


Figure 1 - Electron micrographs of particles from nitrate solutions at $[\text{Zn}^{2+}]_0 = 0.05\text{M}$, $\text{pH}=2$ and

- a) - $T=70^\circ\text{C}$ and $[\text{TAA}]_0 = 0.4\text{M}$ after aging for 1 hr.
- b) - $T=80^\circ\text{C}$ and $[\text{TAA}]_0 = 0.2\text{M}$ after aging for 1 hr.
- c) - $T=80^\circ\text{C}$ and $[\text{TAA}]_0 = 0.4\text{M}$ after aging for 1 hr.
- d) - $T=70^\circ\text{C}$ and $[\text{TAA}]_0 = 0.4\text{M}$ at an early stage of aging.

Polycrystalline nature of spherical particles is clearly seen in the transmission electron micrograph (Figure 1d) taken at an early stage of aging process. XRD patterns of the powders were identical to that of sphalerite and did not contain any indication of a second crystalline phase.

When the precipitation reaction was carried out in the presence of sulfate ions, nucleation was delayed as compared to nitrate system under similar conditions. For example, at $\text{pH}=2$, $T=60^\circ\text{C}$ and $[\text{TAA}]=0.4\text{M}$, it took about 13 minutes for sulfate solution to nucleate as opposed to 8 minutes for nitrate solution. Equilibrium calculations indicated that 15% of zinc ions be tied up in sulfate solutions due to complex formation (3% in nitrate solutions) and that the delay in nucleation is a result of lower free zinc ion concentration.

ZnS particles precipitated in sulfate solutions had a significantly different morphology than those formed in other systems. Under those conditions leading to low rates of sulfide ion generation monosized particles of $3\mu\text{m}$ diameter were obtained as shown in Figure 2a. In this case, only, XRD pattern indicated existence of some

wurtzite phase in addition to sphalerite. However, no attempt was made to determine the relative amounts of these crystalline phases. This agrees well with the observations of Williams et. al. [5] where they concluded that 20% of the mixture was wurtzite. At increased sulfide ion generation rates second generation of particles appeared (Figure 2b) at comparable times to those yielding monosize (3 μ m) particles. Upon elongated aging time, very agglomerated powders were obtained (Figure 2c).

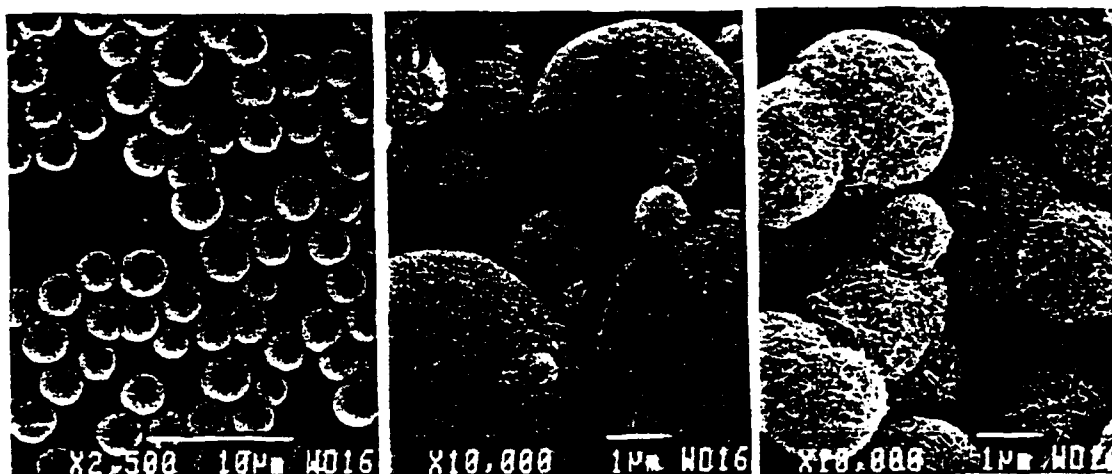


Figure 2 - Scanning electron micrograph of ZnS particles obtained from sulfate solutions with $[Zn^{2+}]_0 = 0.05M$, and

- a) - $T=70^{\circ}C$, $pH = 1$ and $[TAA]_0 = 0.2M$ after aging for 1 hr.
- b) - $T=70^{\circ}C$, $pH = 2$ and $[TAA]_0 = 0.4M$ after aging for 1 hr.
- c) - $T=70^{\circ}C$, $pH = 2$ and $[TAA]_0 = 0.4M$ after aging for 1.5 hr.

Powders precipitated at high sulfide ion generation rates and in the presence of sulfate ions were composed only of sphalerite phase. The fibrous texture is believed to be nuclei that elongated before they attached on the growing particles. However, it remains a mystery how a cubic structure may end up with a fibrous structure.

Although, acetate ions are as good a complex former as sulfate ions, at a pH of 2, $T=60^{\circ}C$ and $[TAA]=0.4M$ precipitation in acetate solutions started earlier than "inert" nitrate solutions. Obviously presence of acetate ions either catalyses the thioacetamide decomposition or forms intermediate species with zinc ions which facilitates attachment of ions to subcritical nuclei. The concentration of undecomposed thioacetamide was followed with a UV-Vis spectrophotometer at 261 nm and compared with the expected concentration calculated from rate expression given by Swift [7]. It has been found that experimentally determined concentration strictly follows calculated values. FTIR spectra of ZnS powders prepared from acetate solutions did not contain any peaks indicating involvement of an intermediate species in the solid phase. Thus it is difficult to explain the observed unanimously early nucleation from acetate solutions

When prepared from acetate solutions, particle morphology did not vary considerably with experimental parameters. Spherical monosized particles of β -ZnS were obtained with all combinations of experimental variables investigated as shown in Figure 3.

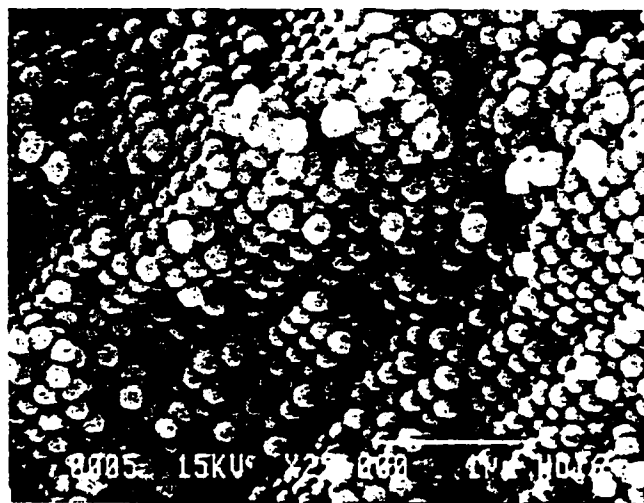


Figure 3 - Scanning electron micrograph of particles obtained by aging for 1 hr. in acetate solution with $[Zn^{2+}]_0 = 0.05M$, $pH=2$, $T=70^\circ C$ and $[TAA]_0 = 0.4M$.

Powders prepared from chloride solutions yielded monosized particles in a very narrow range of experimental parameters leading to intermediate sulfide ion generation rates. Particle characteristics were similar to those from nitrate solutions. In all other cases highly agglomerated powders were obtained.

CONCLUSIONS

Mean ZnS particle size and type of particle size distribution were affected by the sulfide ion generation rate for all anion solutions except acetate. Depending on the sulfide ion generation rate, monosized, bimodal or continuous size distribution was observed. Nitrate, chloride and acetate solution produced submicron particles while sulfate solutions produced particles up to $3\ \mu m$ in diameter in the range of variables studied. Particles from sulfate solutions had a unique fibrous texture which was not apparent in other systems. Acetate ions appeared to hasten nucleation, yet growth was slow compared to other systems.

Powder morphology was more easily controlled in nitrate solutions and the powder characteristics obtained i.e. mean size and phase purity were superior to powders from other anion solutions.

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