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# Preparation and characterization of monoclinic sulfur nanoparticles by water-in-oil microemulsions technique

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**Abstract**

Nanosized monoclinic sulfur particles have been successfully prepared via the chemical reaction between sodium polysulfide and hydrochloric acid in a reverse microemulsions system, with theolin, butanol, and a mixture of Span80 and Tween80 (weight ratio 8 : 1) as the oil phase, co-surfactant and surfactant, respectively. Transparent microemulsions were obtained by mixing the oil phase, surfactant, co-surfactant, and the aqueous phase in appropriate proportion using an emulsification machine at the room temperature. The resulting sulfur nanoparticles were characterized by dynamic light scattering (DLS), X-ray diffraction (XRD), infrared spectroscopy (IR) and transmission electron microscopy (TEM).


*Keywords:* Reverse microemulsions; Sulfur; Nanoparticles

## 1. Introduction

The preparation and characterization of nanoparticles have attracted considerable interest for their peculiar quantum-size properties and high specific surface areas [1–4]. Some methods have been developed to control the size of nanoparticles, for instance, vesicles [5], Langmuir–Blodgett films [6], surface-active supports [7], and reverse microemulsions [8] etc. Microemulsions have been intensively used as spatially constrained micro-reactors to control the growth of inorganic materials and is drawing more and more attention [9–11]. Water-in-oil (W/O) microemulsions are isotropic and thermodynamically stable mixtures consisting of nanosized aqueous droplets, which are surrounded by a monolayer of surfactant molecules dispersed in a continuous non-polar organic medium. Microemulsion system thus can provide a proper microenvironment for the formation of non-aggregated nanoparticles [12–14]. Therefore, microemulsion approach is a promising method for the preparation of nanosized particles.

Sulfur is a chemically and biologically active element, and is widely used in many fields, such as the production of sulfuric acid, chemistry fiber, chemical fertilizer, and rubber, pharmaceutical industry, and bioleaching processes etc. [15]. The size of sulfur particles is an important factor affecting their properties and utilizations. Chemistry vapor deposition (CVD) is a primary method for the preparation of sulfur particulate in the past [16]. By using template-free technology etc., sulfur microtubules and sulfur films were prepared successfully [17 18]. In the present work, we describe the preparation of nanosized sulfur particles in reverse microemulsion systems. The W/O microemulsions, used in the preparation, consist of the following components: butanol, a mixture of Span80 and Tween80, theolin, and water solutions of both sodium polysulfide and hydrochloric acid (HCl).

## 2. Experimental

### *2.1. Materials*

Sulfur powder (20–50 μm) was sublimed sulfur. Sodium sulfide, Span80, Tween80, theolin, butanol, hydrochloric acid and acetone were of reagent grade. The water used throughout this work was the distiller water. Hitachi-8100IV transmission electron microscope (TEM), Siemens D5005 X-ray diffractometer (XRD), Ominic system 2000 infrared spectroscope (IR), and MALVERN Zeta-size 3000HSA analyzer.

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Table 1
Compositions of microemulsion systems

| | Microemulsions I | Microemulsions II |
|---|---|---|
| Aqueous phase | 2 mol/L $Na_2S_x$ : 25 ml | 4 mol/L HCl : 25 ml |
| Surfactant | S and T : 60 g | S and T : 60 g |
| Co-surfactant | Butanol : 10 ml | Butanol : 10 ml |
| Oil phase | Theolin : 450 ml | Theolin : 450 ml |

### *2.2. Particles synthesis*

#### *2.2.1. Preparation of sodium polysulfide solution*

Stock sulfur powder was ground fully in a mortar to form particles of about 5 μm. 12.8 g of grounded sulfur powder was added into a flask that has been filled with 100 ml of sodium sulfide solution (2 mol/L). The reaction was performed at room temperature for 30 min under stirring. The color of the solution changed slowly to orange-yellow with the dissolving of sulfur and sodium polysulfide ($Na_2S_x$) solution was obtained.

$$(x-1)S + Na_2S \rightarrow Na_2S_x$$

#### *2.2.2. Preparation of microemulsions*

In order to prepare reverse microemulsions, theolin, a mixture of Span80 and Tween80 (S&T), butanol and water was used as oil phase, surfactant, co-surfactant and aqueous phase, respectively. The two compositions of the surfactant had a fixed weight ratio (Span80 : Tween80 = 8 : 1). A typical preparation of clear microemulsions of sodium polysulfide (microemulsion I) and hydrochloric acid (microemulsion II) were described below. 60 g of S&T and 10 ml of butanol were added into 450 ml of theolin under stirring to form an organic mixture. Just after this organic mixture was well distributed, 25 ml of sodium polysulfide solution or hydrochloric acid solution was added in it at room temperature. Then transparent reverse microemulsion I or II were obtained by agitating the mixture using an emulsification machine.

#### *2.2.3. Synthesis of sulfur nanoparticles*

An appropriate amounts of microemulsion I and II were mixed together, leading to the formation of insoluble sulfur particles. After reaction, acetone was added to break the steady microemulsion system and cause the sedimentation of the synthesized sulfur particles. The precipitate was separated by centrifugation at 4000 r/min for 15 min. Then it was repeatedly washed with acetone and distilled water to remove oil, surfactant and co-surfactant. Finally, the precipitate was dried in vacuum at 80 for 2 h. The product was light yellow powder. The following chemical reaction occurred in the droplets of the microemulsions when microemulsions I and II were mixed together:

$$Na_2S_x + 2\,HCl \rightarrow 2\,NaCl + H_2S + (x-1)S$$

### *2.3. Characterization*

The product was characterized by X-ray diffraction (XRD) using Siemens D5005 X-ray diffractometer equipped with graphite monochromatized CuKa radiation ($\lambda = 1.5418$ Å), employing a scanning rate of 0.05°/s in the 2θ range from 10° to 70°. Particle distribution was obtained by dynamic light scattering (DLS) using MALVERN Zeta-size 3000HSA analyzer. The size and shape of particles were observed under a Hitachi-8100IV transmission electron microscope (TEM) at 100 kV. The samples for TEM measurement were prepared by deposition of an ultrasonically dispersed suspension of the sulfur product in ethyl alcohol on a carbon-coated copper grid. Infrared (IR) spectra were recorded by Ominic system 2000 Infrared spectroscope employing a potassium bromide (KBr) pellet method.

## 3. Results and discussion

### *3.1. Preparation of microemulsions system*

The studied microemulsions are based on five components: theolin, Span80, Tween80, butanol and water. Clear or turbid microemulsions of sodium polysulfide and hydrochloric acid have been obtained depending on the relative quantities of the components. The use of clear and turbid microemulsions led to different sizes of the resulting sulfur particles. For clear microemulsions, the ratio of theolin : S&T : butanol : water is 90 : 12 : 2 : 5 (ml/g/ml/ml). Aqueous phase of sodium polysulfide solution and hydrochloric acid solution are contained in microemulsions I and II, respectively. Micro-droplets containing aqueous phase in both microemulsion systems can be regarded as nanoreactors, in which sodium polysulfide or hydrochloric acid are soluble and steady. When the above two kinds of reactors collide with each other, a certain reaction occurs and sulfur nanoparticles can form. Table 1 shows the compositions of the microemulsions.

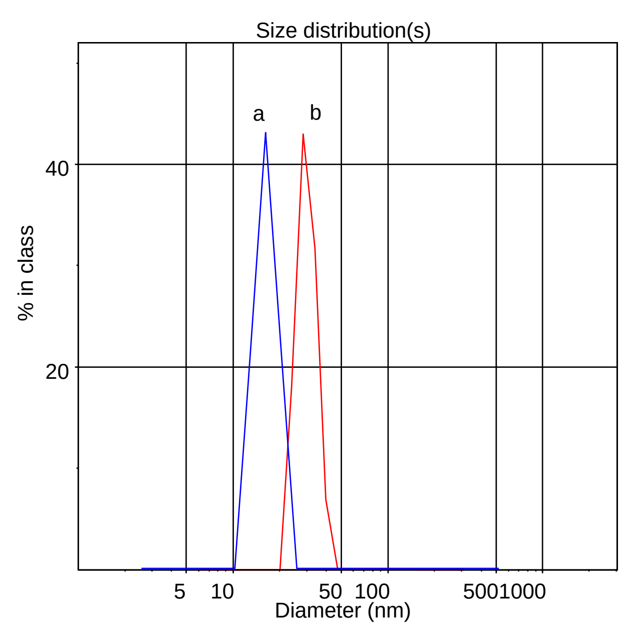


Fig. 1. Size distribution of the sulfur nanoparticles (a) Sodium polysulfide as inorganic reactant, and (b) Ammonium polysulfide as inorganic reactant.