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Synthesis *in situ* of nanosize silver sulphide semiconductor particles in reverse micelles

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Control of the size of silver sulphide semiconductor particles in functionalized reverse micelles was achieved by changing the water content and intermicellar interactions. Opposite to what it is generally observed in reverse micelles, the size of the crystallites varies linearly with water content from 2 to 10 nm. By changing the intermicellar potential, the size distribution slightly decreases and the stability of the particles with time increases.

1. Introduction

The use of dispersed media to synthesize microparticles *in situ* has made considerable progress in the last few years: reverse micelles [1], Langmuir–Blodgett films [2], zeolite [3], vesicles [4], glass matrices and sol–gel methods [5]. Organo-metallic techniques [6] have also been used to produce nanosize particles. Semiconductor nanocrystals present quantum confinement effects, called Q-dots [7].

Reverse micelles are droplets of water in oil stabilized by a monolayer of surfactant [8]. With sodiun di(2-ethylhexyl) sulfosuccinate, AOT, as surfactant, the micellar system presents two properties very important for coprecipitation reactions:

(a) the droplet size increases linearly with water content, $w = [H_2O]/[AOT]$ [9]; and

(b) due to Brownian motion, some collisions between droplets are efficient and exchange processes between water pools occur.

In this paper it is shown that silver sulphide nanosize semiconductors have been synthesized in reverse micelles. The semiconductor size is controlled by the size of the water content, and varies from 2 to 10 nm. The decrease in attractive interactions between reverse micelles due to change of the bulk solvent induces a decrease in size polydispersity and an increase of particle stability with time. The average size of the particles and the size distribution have been characterized by transmission electron microscopy (TEM).

2. Experimental procedure

2.1. Products

Sodium di(2-ethylhexyl)sulfosuccinate, usually called NaAOT, was obtained from Sigma; isooctane was obtained from Fluka, and sodium sulphide from Janssen. Silver di(2-ethylhexyl)sulfosuccinate, AgAOT, has been prepared as described previously [10].

2.2. Synthesis of Ag_2S nanocrystallites

Preparation is achieved by mixing the reverse micellar system with an aqueous solution containing sodium sulphide, Na_2S. Reverse micellar solution is formed by solubilizing in isooctane an AOT micellar solution containing silver and sodium AOT. For a 0.1 M total concentration of AOT surfactant, the silver $[Ag^+]$ and sulphides $[S^{2-}]$ concentrations are 4×10^{-4} M.

2.3. Apparatus

Optical absorption spectra were collected at room temperature on a Uvikon 931 spectrophotometer.

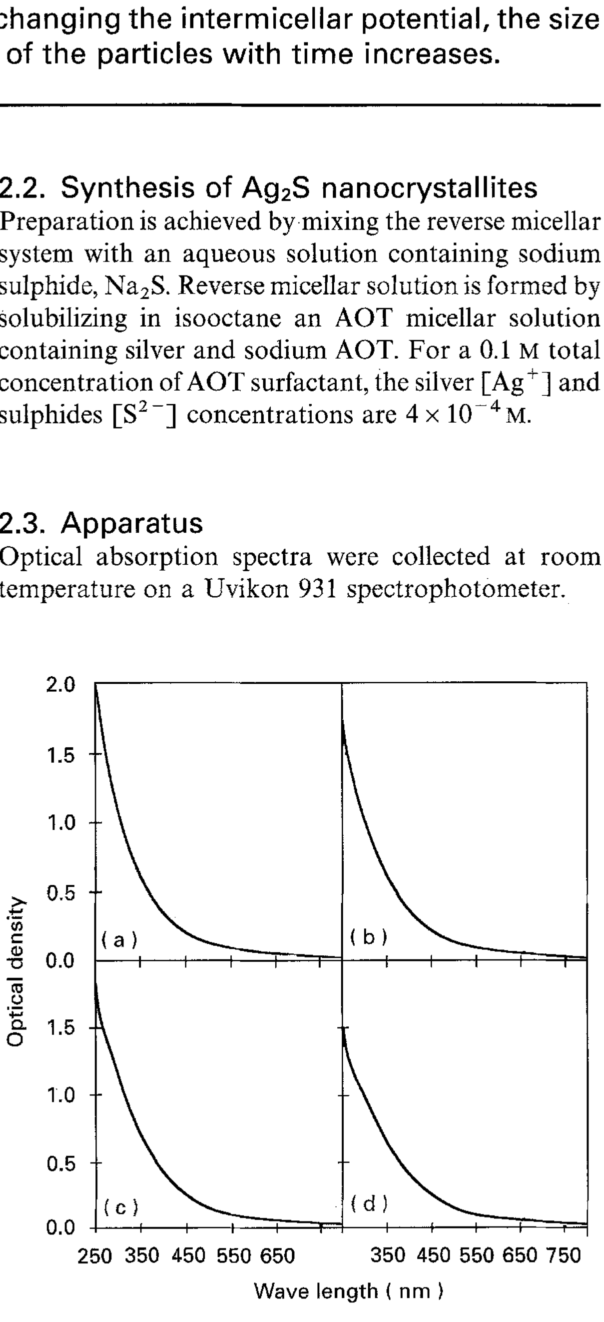

Figure 1 Absorption spectra of Ag_2S synthesized in reverse micelles at various water contents. (a) $w = 5$, (b) $w = 10$, (c) $w = 20$, and (d) $w = 40$, in the system AOTNa–AOTAg–isooctane–water, $[AOT] = 0.1$ M, $[Ag^+] = [S^{2-}] = 4 \times 10^{-4}$ M.

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A Jeol electron microscope, model JEM 100CX II, was used to image nanocrystallites. The samples were prepared by placing a drop of solution on the surface of a copper grid coated with amorphous carbon film.

X-ray diffraction (XRD) measurements were performed with a Stoe–Siemens powder diffractometer, using CuK$_{\alpha}$1 radiation, $\lambda = 0.1542$ nm was used.

3. Results

3.1. Synthesis in reverse micelles

The absorption spectra of Ag_2S synthesized in AOT(Na)–AOT(Ag)–water–isooctane reverse micelles recorded at various water contents, w, are given in Fig. 1. No drastic changes in the absorption spectra with water content, w, is observed. However, a blue shift is obtained compared to the optical band edge of

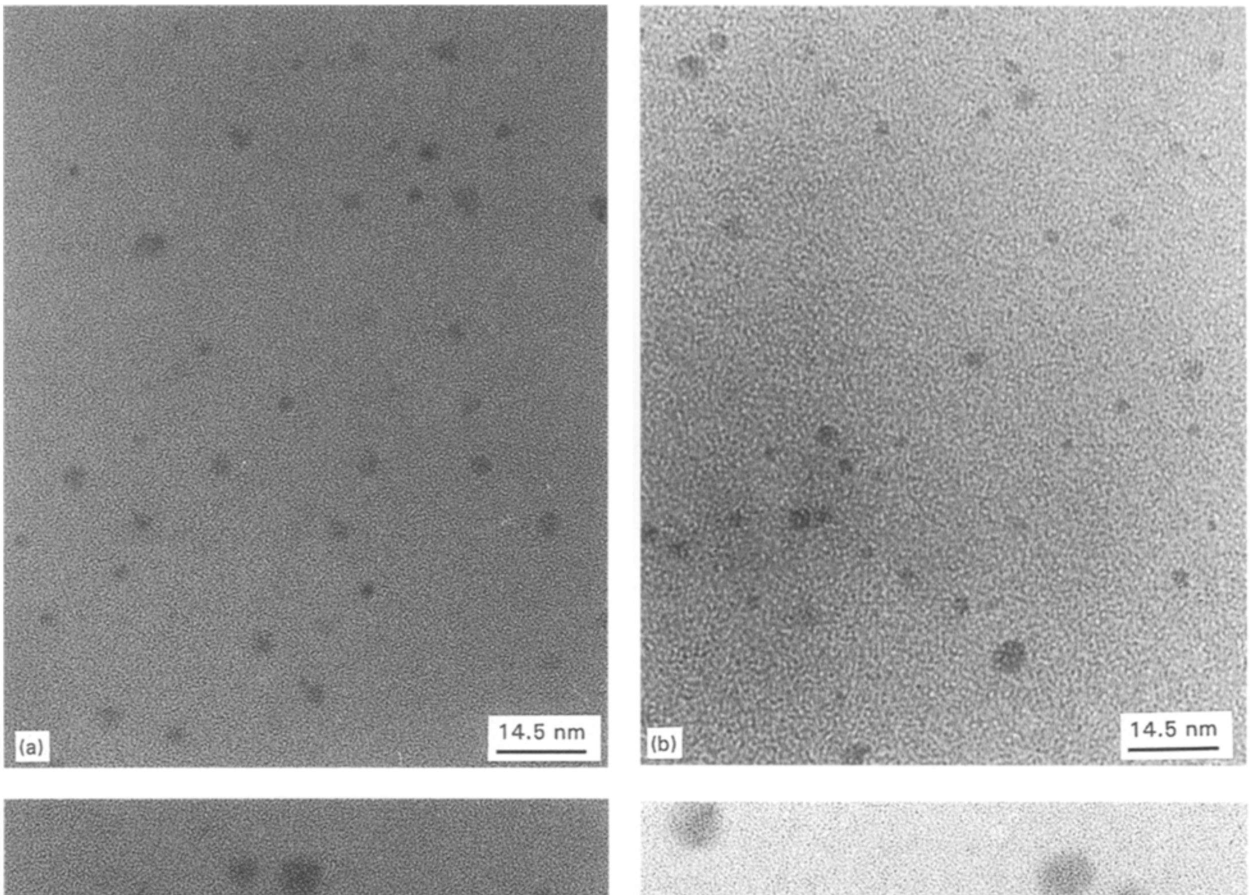

Figure 2 Electron microscopy pictures of Ag_2S synthesized in reverse micelles at various water contents: (a) $w = 5$, (b) $w = 10$, (c) $w = 20$ and (d) $w = 40$.

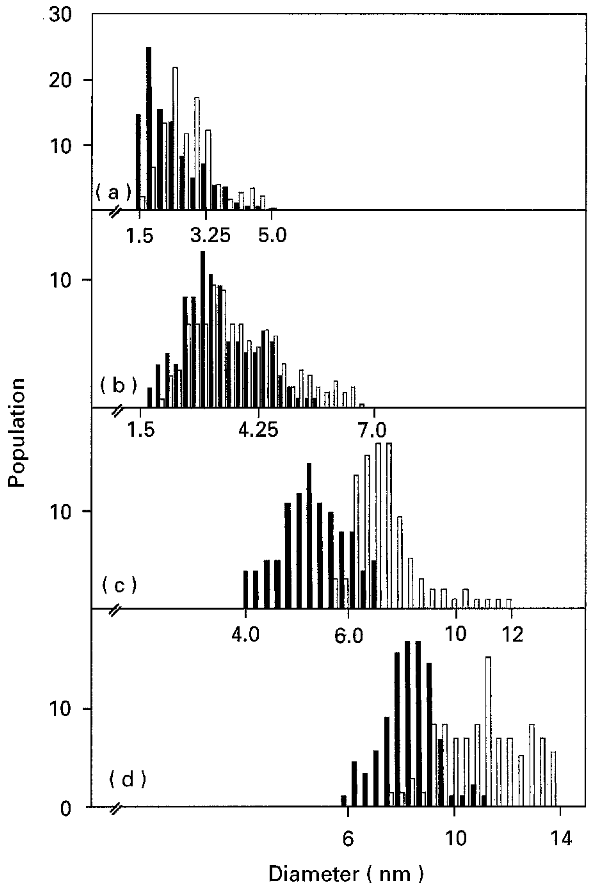

Figure 3 Size distribution of Ag_2S synthesized in reverse micelles at various water contents obtained immediately after synthesis (■) and after 24 h solution ageing (□), at various water contents, *w*. System AOTNa–AOTAg–isooctane–water, [AOT] = 0.1 M, $[Ag^+] = [S^{2-}] = 4 \times 10^{-4}$ M.

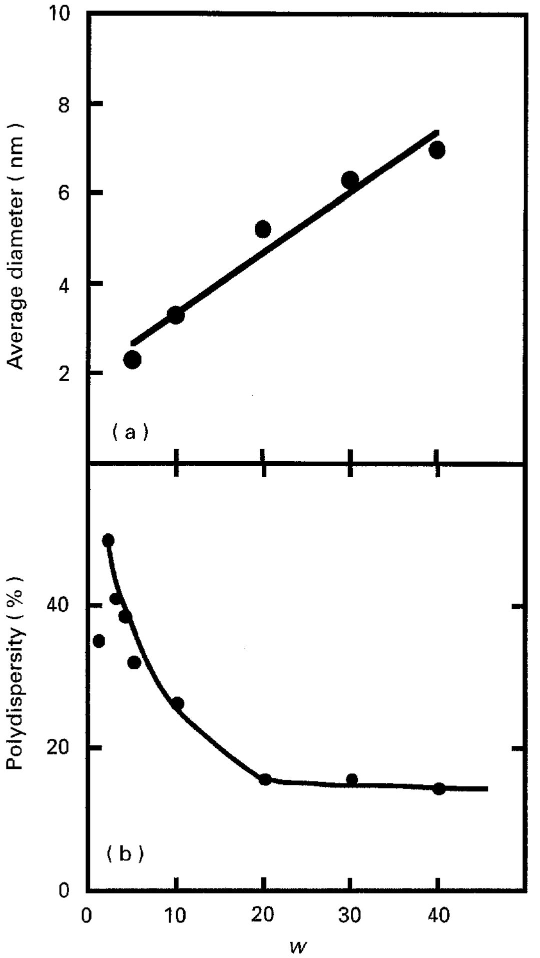

Figure 4 (a) Average diameter of Ag_2S particles with water content, *w*, and (b) variation of size distribution with water content, *w*.

bulk silver sulphide, which is well known to be at 1240 nm (1 eV).

Electron microscopy pictures have been performed following Ag_2S synthesis at various water contents (Fig. 2). Fig. 3 shows histograms obtained by TEM. The size of the Ag_2S particles increases linearly with water content (Fig. 4a) indicating control of crystallite size by the water content. Fig. 4b shows a very large size distribution at low *w* values. It decreases with increasing water content. From high electron microscopic resolution (Fig. 5) it can be observed that the interreticular distance of the lattices indicates good crystallization of Ag_2S particles. The interreticular distance is found to equal 0.26 nm and is attributed to (− 1 2 1) lattices planes.

Bulk silver sulphide [11] exhibits a reversible crystallographic phase transformation at T_c, a critical temperature, 180 °C. The stable phase below T_c is a monoclinic structure and is called β-Ag_2S. Above T_c a cubic phase appears which is called α-Ag_2S. The X-ray diffraction pattern is compared to a simulated diffractogram of the two bulk Ag_2S structures. A good agreement between the experimental and simulated spectra is obtained for the monoclinic structure, β-Ag_2S.

To check the stability of particles with time, the previous solutions were kept in micellar solutions for 24 h. The absorption spectra of Ag_2S nanosize

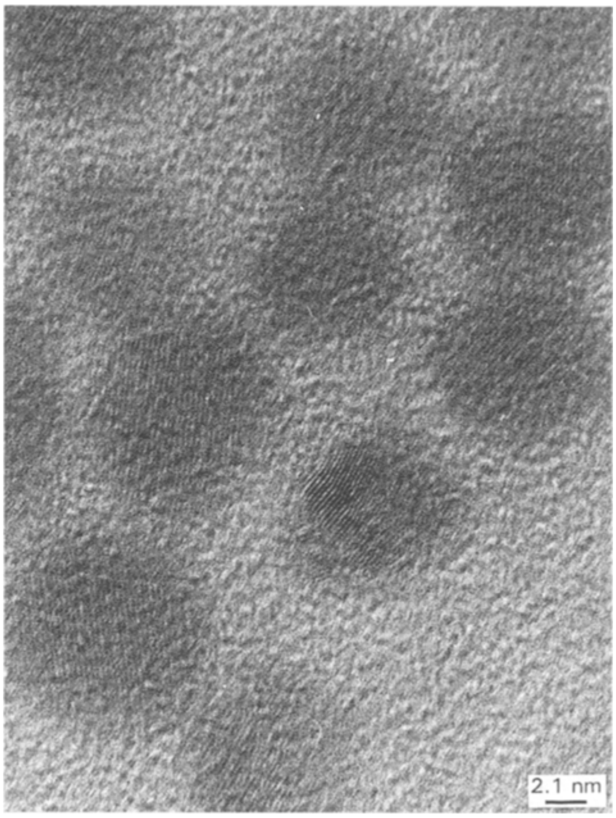

Figure 5 High electron microscopy pattern of Ag_2S synthesized in reverse micelle at *w* = 40.

particles are unchanged compared to that given on Fig. 1. The comparison of histograms obtained immediately and 24 h after the synthesis (Fig. 3) shows an increase in average size with time. The increase in average size with time is limited to 15% at $w = 5$ and 10 and is about 45% at $w = 20$ and 40. However, it can be noticed that there are no drastic changes in polydispersity with time.

3.2. Change in interaction between droplets

The intermicellar potential, deduced from the Baxter model, strongly depends on the bulk solvent [12]. As a matter of fact, it decreases with the number of carbon atoms in the solvent. This has been explained in terms of solvent penetration: bulk solvent molecules having a small number of carbon atoms penetrate easily in the surfactant alkyl chains, which are then well solvated. This decreases intermicellar interaction. The increase in the number of carbon atoms of the bulk solvent induces a decrease in the solvation of the surfactant and then an increase in the intermicellar attractive potential. By replacing isooctane by cyclohexane as the bulk solvent, the intermicellar potential decreases inducing a decrease in the exchange micellar rate, which is constant by a factor of ten [13]. Furthermore, the maximum of water molecules solubilized decreases. By replacing isooctane by cyclohexane, the maximum value of w changes from 40 to 10, respectively.

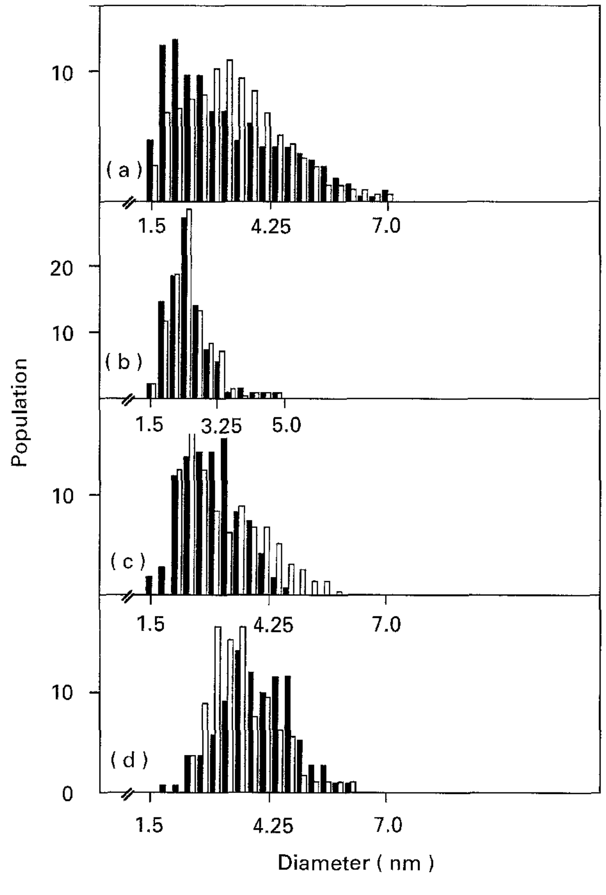

Figure 6 Size distributions of Ag_2S synthesized in reverse micelle having cyclohexane as the bulk solvent, at various water contents, immediately after synthesis (■) and after 24 h solution ageing (□), at various water contents, w: (a) $w = 3$, (b) $w = 5$, (c) $w = 7.5$, and (d) $w = 10$.

Synthesis of Ag_2S has been performed using cyclohexane as the bulk solvent. The data are compared to those given above with isooctane. The absorption spectra of Ag_2S are unchanged compared to those obtained for isooctane (Fig. 1a, b). The average size of the particles does not change compared to that obtained with isooctane (Fig. 6) and increases with water content and with time. However, a decrease in the size distribution with time can be observed, compared to what is obtained by using isooctane as the bulk phase (Fig. 3).

4. Discussion

The absorption spectra of silver sulphide particles (Fig. 1) corresponding to various particle sizes (Fig. 2) do not drastically change with water content. However, a blue shift is obtained compared to the optical band edge of bulk silver sulphide that is well known to be present at 1240 nm (1 eV). The small change in absorption spectra and band gap with particle size is rather surprising. As a matter of fact, a change in the electronic properties is observed when the diameter of the particles approaches the excitonic diameter. This gives a widening of the forbidden band and therefore a blue shift in the absorption threshold as the size decreases. For nanocrystals having a direct gap absorption, sharp absorption onset with multiple discrete features consistent with quantum confinement is observed [14–22]. For indirect transition in nanocrystals, electronic absorption shows no discrete features in the visible–infrared region. However, for particles having an indirect transition, such as PbS or CdSe submitted to high pressure [23], a blue shift compared to the bulk phase with a decrease in particle size is observed. In the case of silver sulphide, a direct and an indirect transition takes place. So, whatever the transition is, one would expect a large change in the energy band gap with particle size. The fact that the absorption and energy band gap do not drastically change with particle size, for a variation of the diameter from 1 to 10 nm cannot be explained easily.

Various syntheses of nanosize materials have been performed in reverse micellar solution (CdS [14–17], $Cd_yZn_{1-y}S$ [24], metallic silver [25] and copper [26, 27] particles). In all cases, an increase in particle size is observed with water content, from $w = 1$ to 15. Above $w = 15$, an unchanged value of the average particle size and an increase in polydispersity is observed.

The behaviour of the change of Ag_2S average size and polydispersity with water content totally differs to that observed for other semiconductors and metallic particles [14–17, 24–27]: that a linear increase in the average size (Fig. 4a) and a decrease in polydispersity (Fig. 4b) with water content are observed. Such changes in the behaviour of the size and polydispersity with w are rather surprising. They could be attributed to the fact that, as opposed to other materials, silver ions need to be hydrated to react with sulphur derivatives. The nucleation process is

$$2n\mathrm{Ag}^{+} + n\mathrm{S}^{2-} \rightarrow (\mathrm{Ag}_2\mathrm{S})_n \qquad (1)$$

At low water content, a very low amount of hydrated silver ions is formed. After mixing, immediately silver and sulphur ions are in contact, but small amounts of nuclei are formed. After nuclei formation, the water used to hydrate silver ions can participate in the formation of other nuclei. Hence, the number of nuclei increases with time inducing various growth processes, with the formation of particles having various sizes. Above $w = 15$, bulk water is present in the microphase and all the silver ions are hydrated. After mixing silver and sulphur ions, all the nuclei are immediately formed and the growth process takes place inducing formation of particles having a small size distribution.

The change in the bulk solvent induces a change in the intermicellar potential, keeping similar droplet size. The unchanged value of silver sulphide average size confirms that the size of the droplets controls the size of the particles.

At low water contents, the size of the particles and polydispersity do not drastically change with time. However, increases in the size and polydispersity are slightly higher when isooctane is used as the bulk solvent compared to cyclohexane.

At high water content, by using isooctane as the bulk solvent, drastic changes in the size and polydispersity are observed. To understand such results the growth process has to be taken into account, which can be expressed as

$$2Ag^+ + S^{2-} + (Ag_2S)_n \rightarrow (Ag_2S)_{n+1} \qquad (2)$$

$$(Ag_2S)_n + (Ag_2S)_k \rightarrow (Ag_2S)_{n+k} \qquad (3)$$

Equation 2 can be neglected because synthesis is performed in excess of sulphur ions. So the concentration of silver ions remaining in the solution is very low because most of them already react with sulphur ions (Equation 1). Hence, the growth of particles with time is mainly due to Equation 3. Such reaction (Equation 3) takes place when droplets filled by clusters collide. However, the probability of such collisions is very low. As a matter of fact, the cluster concentration, which depends on the size of the particles, is very low $\leqslant 10^{-6}$ M) compared to micellar concentration, [M], (10^{-4} M $< [M] < 5 \times 10^{-3}$ M). So, most of the droplets are empty and only a few droplets are filled with clusters. Hence, most of the micellar exchange processes will involve empty droplets.

An increase in the micellar exchange process with increasing water content has been observed [13]. Hence, the growth of particles due to Equation 3 is more efficient at high rather than at low water contents. Similarly, at a given water content, the decrease in intermicellar exchange due to a decrease in the intermicellar potential, slows down the growth of particles; as is observed in cyclohexane compared to isooctane.

5. Conclusions

In the present paper, it has been shown that the size of silver sulphide particles is controlled by the size of water droplets and polydispersity is controlled by the water content. The decrease of the intermicellar exchange process prevents the growth of particles with time.

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