# Hydrochemical Precipitation of Nanocrystalline Lead Sulfide Powders

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**Abstract**—Single-phase nanocrystalline PbS powders have been synthesized from aqueous solutions of lead nitrate and lead acetate, using sodium sulfide as a sulfur source and sodium citrate or Trilon B as a complexing agent. The average particle size of the lead sulfide in the synthesized nanopowders depends on the nature of the complexing agent and its concentration. Our results demonstrate the possibility of controlled precipitation of PbS nanoparticles with a preset size in the range from 5−6 to ≃100 nm.

## INTRODUCTION

The synthesis of semiconducting chalcogenide nanoparticles for electronic, catalytic, and other applications is of great interest. Along with the development of techniques for the preparation of semiconductor nanoparticles, considerable research effort has been concentrated on the possibility of producing nanoparticles of controlled size and shape [1−4].

Bulk lead sulfide (PbS) is a semiconductor with a narrow band gap ($\simeq 0.41$ eV) and a large exciton size ($\simeq 18−24$ nm). The physical and chemical properties of nanocrystalline PbS with a particle (grain) size approaching the exciton size can be modified markedly owing to a size effect [1, 2]. For example, a nanostructured PbS film has a cubic structure ($DO_3$ type) [5−8], in contrast to bulk lead sulfide, which has the $B1$ structure. A reduction in the grain size of a nanostructured PbS film from 80 to 30 nm is accompanied by an increase in its band gap from $\simeq 0.8$ to $\simeq 1.4$ eV [7, 8]. The thermal expansion coefficient of a nanostructured PbS film with a grain size of $\simeq 40$ nm is almost twice that of bulk PbS [9, 10].

Nanocrystalline lead sulfide can be used in electroluminescent devices, solar cells, IR photodetectors, detectors, and switches [11, 12].

The most widespread method for the synthesis of nanocrystalline lead sulfide is chemical precipitation from aqueous solutions, also referred to as one-pot synthesis in aqueous solutions [13, 14]. Previously [15, 16], we reported the synthesis of PbS nanopowders with controlled particle size in the range 5−55 nm from lead acetate and sodium sulfide in the presence of $Na_2$-EDTA or sodium citrate.

In this paper, we examine the effect of initial synthesis conditions on the particle size of PbS in a wide range, from 5 to 100−110 nm, in the synthesis of PbS nanopowders from lead nitrate or acetate, with the use of $Na_2S$ as a sulfur source.

## EXPERIMENTAL

Nanocrystalline PbS powders were synthesized by chemical precipitation from aqueous solutions of lead nitrate or acetate and sodium sulfide. The starting solutions of lead nitrate ($Pb(NO_3)_2$) or lead acetate ($Pb(CH_3COO)_2 \equiv Pb(AcO)_2$) and sodium sulfide ($Na_2S$) had identical concentrations: 0.5 mol/L. The complexing agents used were solutions of disodium salt of ethylenediaminetetraacetic acid (Trilon B, complexone III) or sodium citrate ($Na_3C_6H_5O_7 \equiv Na_3Cit$). Synthesis with the use of Trilon B was carried out with the addition of acetic acid ($CH_3COOH$) or sodium hydroxide (NaOH) and without them. The process was run at a temperature of 298 K. The pH of the solutions during the synthesis was from 3−4 in an acid medium to 12−14 in an alkaline medium. The volume of the reaction mixtures was 200 mL.

The initial $Pb(NO_3)_2$ or $Pb(AcO)_2$ and $Na_2S$ concentrations in all of the reaction mixtures were 0.05 mol/L. The concentrations of the complexing agents (sodium citrate and Trilon B) in the reaction mixtures were varied in the ranges from 0.0125 to 0.05 and 0.015 to 0.065 mol/L, respectively (table). The ratio of the lead and sulfide ion concentrations in all of the mixtures was stoichiometric: $[Pb^{2+}] : [S^{2−}] = 1 : 1$.

To assess the effect of initial conditions on the size of the nanoparticles thus prepared, we carried out syntheses in which the set of reactants and their concentrations in the reaction mixture were varied. PbS has a small solubility product $K_{sp}$ (at a temperature of 298 K,

Initial chemical precipitation conditions and size of PbS nanoparticles prepared according to different reaction schemes

| Reactant concentrations in the reaction mixture, mol/L | | | | | | | $\tau^*$, h | $\langle D \rangle$, nm |
|---|---|---|---|---|---|---|---|---|
| $Pb(NO_3)_2$ | $Pb(AcO)_2$ | $Na_2S$ | Trilon B | $Na_3Cit$ | $CH_3COOH$ | NaOH | | |
| 0.05 | 0 | 0.05 | 0 | 0 | 0 | 0 | 0 | $\simeq 10-15$** |
| 0.05 | 0 | 0.05 | 0 | 0.025 | 0 | 0 | 0 | $6 \pm 1$ |
| 0.05 | 0 | 0.05 | 0 | 0.0125 | 0 | 0 | 0 | $5 \pm 1$ |
| 0.05 | 0 | 0.05 | 0 | 0.02 | 0 | 0 | 120 | $6 \pm 1$ |
| 0.05 | 0 | 0.05 | 0 | 0.05 | 0 | 0 | 0 | $6 \pm 1$ |
| 0.05 | 0 | 0.05 | 0.015 | 0 | 0 | 0 | 24 | $11 \pm 1$ |
| 0.05 | 0 | 0.05 | 0.015 | 0 | 0 | 0 | 72 | $11 \pm 1$ |
| 0.05 | 0 | 0.05 | 0.025 | 0 | 0 | 0 | 24 | $11 \pm 1$ |
| 0.05 | 0 | 0.05 | 0.025 | 0 | 0 | 0 | 72 | $11 \pm 1$ |
| 0.05 | 0 | 0.05 | 0.035 | 0 | 0 | 0 | 24 | $11 \pm 1$ |
| 0.05 | 0 | 0.05 | 0.035 | 0 | 0 | 0 | 72 | $12 \pm 2$ |
| 0.05 | 0 | 0.05 | 0.05 | 0 | 0 | 0 | 0 | $21 \pm 3$ |
| 0.05 | 0 | 0.05 | 0.065 | 0 | 0 | 0 | 120 | $78 \pm 3$ |
| 0.05 | 0 | 0.05 | 0.065 | 0 | 0 | 0 | 0 | $69 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.035 | 0 | 0 | 0 | 24 | $38 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0 | 0 | 0 | $45 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.05 | 0 | 0 | $56 \pm 4$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.10 | 0 | 0 | $48 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.10 | 0 | 24 | $55 \pm 2$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.10 | 0 | 48 | $56 \pm 2$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.25 | 0 | 0 | $40 \pm 2$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.25 | 0 | 24 | $48 \pm 2$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.25 | 0 | 48 | $49 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0.05 | 0 | 120 | $70 \pm 5$ |
| 0 | 0.05 | 0.05 | 0.065 | 0 | 0 | 0 | 120 | $86 \pm 12$ |
| 0 | 0.05 | 0.05 | 0.065 | 0 | 0.05 | 0 | 0 | $64 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.065 | 0 | 0.05 | 0 | 72 | $59 \pm 4$ |
| 0 | 0.05 | 0.05 | 0.065 | 0 | 0.05 | 0 | 120 | $88 \pm 2$ |
| 0 | 0.05 | 0.05 | 0.10 | 0 | 0.05 | 0 | 120 | $95 \pm 10$ |
| 0 | 0.05 | 0.05 | 0.10 | 0 | 0.15 | 0 | 120 | $95 \pm 10$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0 | 0.05 | 0 | $27 \pm 1$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0 | 0.10 | 0 | $35 \pm 3$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0 | 0.15 | 0 | $32 \pm 2$ |
| 0 | 0.05 | 0.05 | 0.05 | 0 | 0 | 0.25 | 0 | $33 \pm 2$ |

\* Residence time of the precipitated PbS powder in the matrix solution.

\*\* The precipitated PbS powder contained $PbSO_4$ as a sulfate impurity phase, so the particle size of the lead sulfide was evaluated only roughly.

$K_{sp} = 2.5 \times 10^{-27}$ [17] or $8.0 \times 10^{-28}$ [18]), so, at a sufficient $Na_2S$ concentration in the reaction mixture, PbS formation takes just $1-2$ s. As a result, the reaction mixture first blackens. Next, PbS particles precipitate, and the solution becomes transparent. The precipitation of the PbS nanoparticles takes $\simeq 1$ h. Faster precipitation, taking $5-10$ min, is observed in the case of nanoparticle agglomeration. Immediately after the precipitation, the precipitate was washed with distilled water by decantation, filtered off, and dried in air at a temperature of 323 K. In addition, we examined the effect of the residence time $\tau$ of the precipitate in the
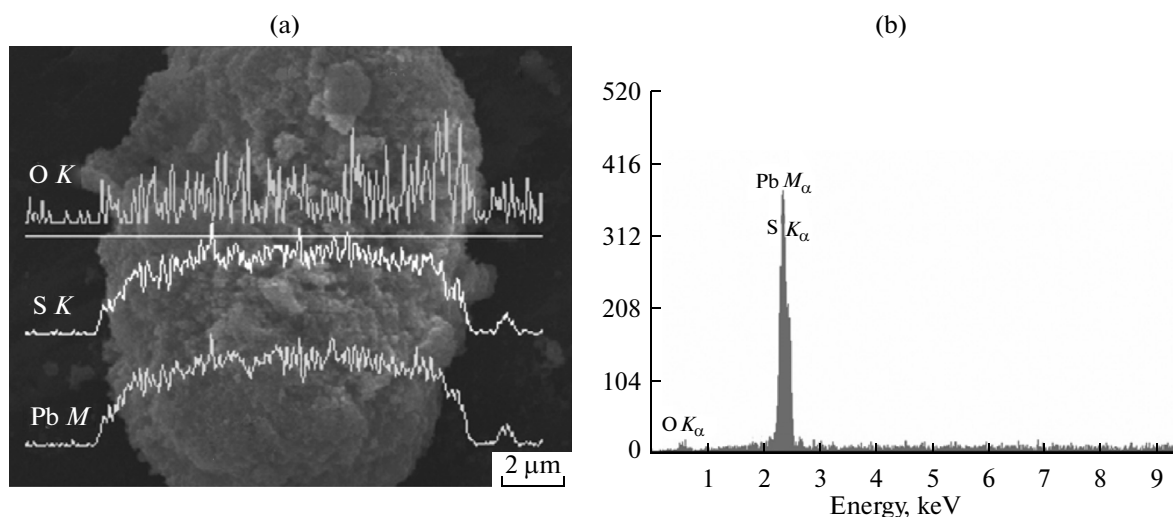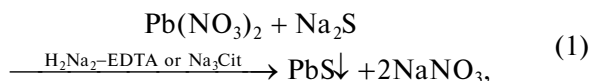
(a)                                                              (b)



**Fig. 1.** (a) Pb, S, and O concentration profiles determined by EDX spectrometry in PbS nanopowder synthesized from Pb(AcO)$_2$, Na$_2$S, and Trilon B: agglomerated PbS particle; in addition to the Pb, S, and O concentration profiles determined by EDX spectrometry, the scan direction across the agglomerate is shown (white horizontal line); (b) elemental composition of the agglomerate.

matrix solution on the particle size of the PbS. The residence time of the already precipitated PbS particles in solution was varied from 1 to 120 h (table).

Lead sulfide precipitation followed the reaction schemes

$$Pb(NO_3)_2 + Na_2S$$
$$\xrightarrow{\text{H}_2\text{Na}_2\text{–EDTA or Na}_3\text{Cit}} PbS\downarrow + 2NaNO_3, \quad (1)$$

$$Pb(AcO)_2 + Na_2S \xrightarrow{\text{H}_2\text{Na}_2\text{-EDTA}} PbS\downarrow + 2NaOAc. \quad (2)$$

The process was run in the following sequence: after adding a complexing agent to lead nitrate or acetate, the volume of the mixture was brought to 100 mL and the resultant solution was mixed with 100 mL of a Na$_2$S solution.

All of the precipitated powders were characterized by X-ray diffraction on a Shimadzu XRD-7000 diffractometer with Cu$K_{\alpha_{1,2}}$ radiation ($2\theta = 20°-95°$, scan step $\Delta(2\theta) = 0.03°$, counting time per data point of 10 s). X-ray diffraction patterns were analyzed numerically using the X'Pert Plus software package [19].

The average particle size $\langle D \rangle$ (average crystallite size) of the synthesized lead sulfide powders was determined from the broadening of diffraction line profiles using the dependence of the reduced broadening of the reflections, $\beta^*(2\theta) = [\beta(2\theta)\cos\theta]/\lambda$, on the scattering vector $s = (2\sin\theta)/\lambda$ [15, 20].

The microstructure of the powders was examined by scanning electron microscopy (SEM) on a JEOL JSM-6390 LA equipped with a JED 2300 energy dispersive X-ray analyzer.

## RESULTS AND DISCUSSION

The initial synthesis conditions and particle size of all PbS nanopowders are summarized in the table. Consider the experimental data obtained in this study.

X-ray diffraction results indicate that, independent of the particle size, all of the synthesized PbS powders have a cubic structure (*B*1 type) with a lattice parameter $a_{B1} = 0.592-0.594$ nm, in agreement with previous data [14, 21, 22].

According to energy dispersive X-ray (EDX) spectrometry data, the Pb, S, and O contents of the synthesized, dried, single-phase lead sulfide powders were $86 \pm 2$, $13 \pm 1$, and $1 \pm 0.5$ wt %, respectively. EDX spectrometry results (Fig. 1) showed that the oxygen was distributed over the surface of the particles. Annealing was accompanied by a decrease in the oxygen content of the powders from $\simeq 4.1$ to $\simeq 1.0-1.5$ wt %. Annealing led to water removal from the powders. Therefore, most of the oxygen present in the powders corresponded to adsorbed water, and the rest was chemisorbed water.

Figure 2 shows X-ray diffraction patterns of the nanocrystalline PbS powders with the smallest and largest particle sizes and illustrates how the particle size was evaluated from the broadening of diffraction line profiles. The finest nanopowder, with an average particle size of 5 nm, was synthesized by the reaction scheme (1) using lead nitrate, sodium sulfide, and sodium citrate with concentrations of 0.05, 0.05, and 0.0125 mol/L, respectively. The nanopowder with an average particle size of 95 nm was synthesized by the reaction scheme (2) using a mixture of lead acetate, sodium sulfide, Trilon B, and acetic acid with concentrations of 0.05, 0.05, 0.10, and 0.05 mol/L, respectively. Diffraction line broadening analysis showed
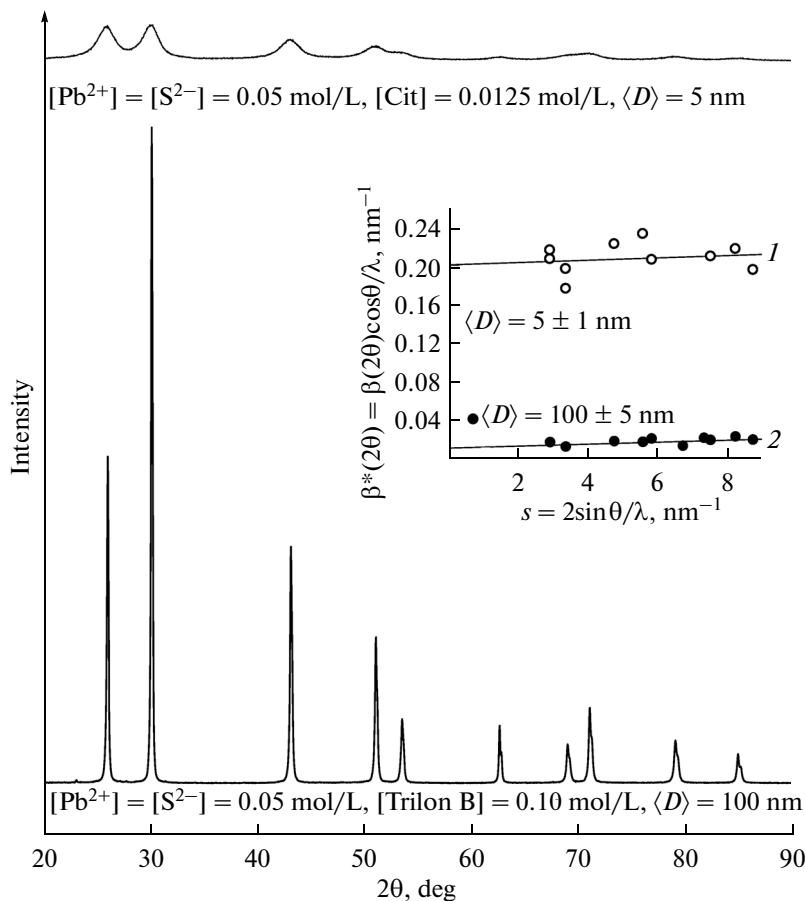
**Fig. 2.** X-ray diffraction patterns of PbS nanopowders with a particle size of 5 (top scan) and 95 nm (bottom scan). Inset: reduced broadening $\beta^*(2\theta)$ of diffraction line profiles as a function of scattering vector $s$ for the synthesized PbS powders: (*1*) synthesis from a mixture of $Pb(NO_3)_2$, $Na_2S$, and $Na_3Cit$ with concentrations of 0.05, 0.05, and 0.0125 mol/L, respectively; (*2*) synthesis from a mixture of $Pb(AcO)_2$, $Na_2S$, Trilon B, and acetic acid with concentrations of 0.05, 0.05, 0.10, and 0.05 mol/L, respectively. The solid lines represent fits to the experimental $\beta^*(s)$ data.

that the internal strain in the powders thus prepared was very low, no greater than 0.1%, that is, within experimental uncertainty.

The finest PbS nanopowders, with an average particle size in the range 5–15 nm, were obtained by reacting mixtures of $Pb(NO_3)_2$ and $Na_2S$, using sodium citrate as a complexing agent. Varying the $Na_3Cit$ concentration in the range from 0.0125 to 0.05 mol/L had no effect on the average particle size of PbS to within uncertainty in our measurements. Lead sulfide synthesis from $Pb(NO_3)_2$ and $Na_2S$ with no complexing agent led to PbS precipitation together with $PbSO_4$ as an impurity phase. When Trilon B was used instead of $Na_3Cit$, coarser nanopowders precipitated from reaction mixtures of $Pb(NO_3)_2$ and $Na_2S$ (table). In previous work [15, 16], synthesis from reaction mixtures of $Pb(AcO)_2$ and $Na_2S$ with the use of sodium citrate also led to the formation of fine PbS nanoparticles 5–10 nm in size. Increasing the Trilon B concentration in the reaction mixture leads to the precipitation of larger nanoparticles. The particle size of

PbS in precipitated nanopowders also increases as the residence time $\tau$ of the precipitate in the matrix solution increases from 0 to 120 h (table).

The precipitation of lead sulfide from reaction mixtures of $Pb(AcO)_2$, $Na_2S$, and Trilon B in an alkaline medium (with the addition of NaOH) with pH > 8 allowed us to obtain PbS nanoparticles no greater than 35 nm in size, whereas synthesis in an acid medium (with the addition of acetic acid) resulted in the formation of PbS nanoparticles 50–60 nm and more in size.

Holding a precipitated nanopowder in an acid matrix solution for many hours caused the nanoparticles to form agglomerates, in which the particles experienced coalescence and further growth. For example, in the PbS powder that was precipitated from a reaction mixture of lead acetate, sodium sulfide, Trilon B, and acetic acid with concentrations of 0.05, 0.05, 0.05, and 0.25 mol/L, respectively, and then held in the matrix solution for 48 h, we detected agglomerates up to 300–400 nm in size, in which the formation of par-
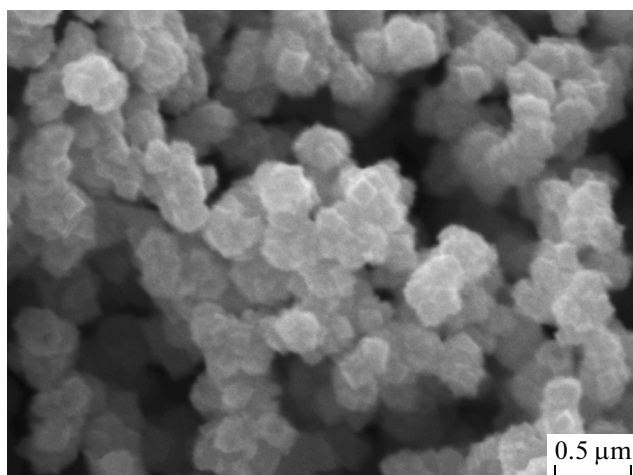
0.5 μm

**Fig. 3.** Microstructure of an agglomerated PbS nanopowder after 48 h of holding in the matrix solution. Agglomerates up to 300−400 nm in size are seen, in which coalescence of the nanoparticles and the formation of particles with cubic morphology are observed to begin.
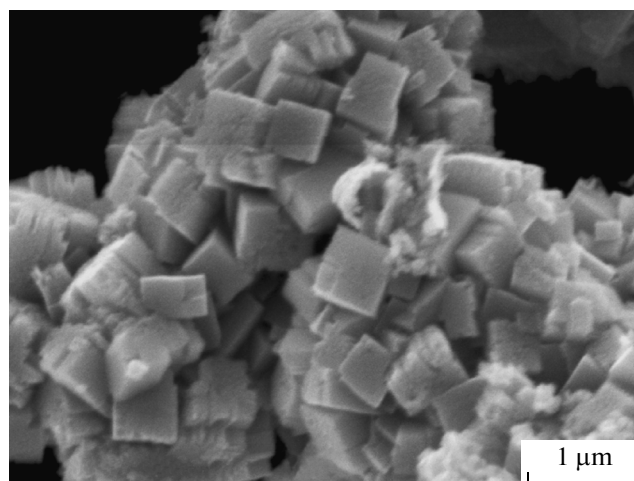


1 μm

**Fig. 4.** Scanning electron microscopy image of PbS powder after 120 h of holding in the matrix solution. The powder is seen to consist of well-faceted lead sulfide particles with cubic morphology, 400−500 nm in size.

ticles with cubic morphology was observed to begin (Fig. 3). According to X-ray diffraction data, the crystallite size in this powder was about 50 nm (table).

Increasing the residence time of the precipitated PbS powder in the matrix solution to 120 h led to the formation of well-faceted particles with cubic morphology, 400−500 nm in size (Fig. 4). The powder was precipitated from a mixture of lead acetate, sodium sulfide, Trilon B, and acetic acid with concentrations of 0.05, 0.05, 0.10, and 0.15 mol/L, respectively. According to X-ray diffraction data, the crystallite size in this powder was about 100 nm (table).

On the whole, scanning electron microscopy results, together with the crystallite sizes evaluated by X-ray diffraction, attest to severe agglomeration of the lead sulfide powders. One possible cause of the agglomeration is that the surface of the synthesized PbS nanoparticles is hydrophobic.

Precipitation from aqueous solutions allowed us to synthesize PbS nanopowders essentially free of lattice strain.

## CONCLUSIONS

The particle size of lead sulfide prepared by precipitation from aqueous solutions of lead nitrate and lead acetate, using sodium sulfide as a sulfur source, depends on the nature of the complexing agent and its concentration. Varying these parameters at a temperature of 298 K, one can tune the particle size of PbS in the range from 5 to 90−100 nm. The finest PbS powders, consisting of nanoparticles 5−6 nm in size, can be synthesized using sodium citrate as a complexing agent. All other factors being equal, the use of Trilon B as a complexing agent leads to the precipitation of nanoparticles 12 nm and more in size. Therefore, it is reasonable to use sodium citrate as a complexing agent for the targeted synthesis of PbS nanoparticles less than 10 nm in size and Trilon B for the preparation of larger nanoparticles, up to 100 nm in size.

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