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PbS Sub-micrometer Structures with Anisotropic Shape: Ribbons, Wires, Octapods, and Hollowed Cubes

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The current paper discusses the preparation, characterization, and clarification of the growth mechanism of PbS wires, ribbons, octapods, and hollowed cubes. Those sub-micrometer structures were prepared by a thermal decomposition of a uni-precursor $\{[Pb(S_2CNEt_2)_2]_2\}$, using either ethylene diamine (en) or ethylene glycol (eg) as an intermediate reagent, as well as surfactants. The growth in eg produced mainly ribbons and square plates, while the growth in en solutions produced wires at the lower temperatures (80 °C) and octapods and hollowed cubes at elevated temperatures (117 °C). The experimental observations suggest that the obtained morphologies are primarily determined by the nucleation phase and the subsequent growth kinetics. The growth process developed according to the characteristic habit and subsequent branching processes. The characteristic habit was controlled by the surface energy of the facets and their modulation by the solvent molecules. The branching process was determined by a delicate balance between kinetic and thermodynamic processes, and it was controlled by the variation of the temperature and duration of the reactions.

I. Introduction

The sub-micrometer structures of lead sulfide (PbS), belonging to the IV−VI semiconductor family, exhibit unique physical properties emanating from the intrinsic nature of the bulk materials. A bulk PbS is a direct band gap semiconductor with a small band gap (0.41 eV at 300 K), small effective mass of the electron, and hole ($0.1m_0$) and a relatively large exciton Bohr radius (18 nm). These properties endow the sub-micrometer structures of PbS, including the micrometer and nanometer sized crystals, with a good electrical conductivity, a quantum confinement of the carriers and an optical tunability in the near infrared spectral regime. In consequence, the PbS sub-micrometer structures were already found to be useful in various opto-electronic devices, including light-emitting diodes,[1,2] electroluminescence devices,[3] optical switches,[4] and solar cells.[5]

The fabrication of PbS semiconductors with well determined size is already well established;[6,7] however, the control of the shape is still a major concern and presents a prime challenge for the near future, since the chemical and physical properties of sub-micrometer structures can be strongly determined by their shape.[8] During the past decade, a few attempts explored the possibility to control the shape of the sub-micrometer structures, including the use of a gas-phase synthesis, such as vapor−liquid−solid (VLS) and thermal evaporation methods.[9−11] Some advanced structures, such as wires, ribbons, and tubes have been demonstrated.[12−16]

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Alternatively, a colloidal approach was proposed a few years ago with the pioneering synthesis of CdSe nanorods,[17] enabling a convenient and reproducible route for the fabrication of structures with a controlled size and shape, as well as facilitating the ease of dispersing them in organic or aqueous media for the numerous applications in optoelectronics, electronics, and biological systems.

Spherical nanocrystals of the IV−VI semiconductors were prepared in the past decade, using simple chemical procedures, including a growth in a polymer[18] or zeolites,[19] inverse micelle,[20] and under the influence of γ-irradiation.[21] In addition, a successful colloidal method was developed in recent years for the formation of spherical and monodispersed PbS and PbSe nanocrystals with high crystalline properties.[6]

The preparation of anisotropic structures has been developed only in recent years. Rods and wires of PbS and PbSe crystals were prepared by using ethylene diamine (en) as a coordinating and templating ligand.[22,23] Rectangular and rodlike PbS crystals have been prepared either by solvothermal reaction or in organic N-chelating solvents.[24] Closed PbS nanowires were achieved using a solvothermal process.[25] PbS dendrites have been synthesized via a hydrothermal or solvothermal methods.[26,27] PbS sub-micrometer structures in highly faceted star shapes, truncated octahedrons, and cubes have been fabricated recently.[28]

This paper discusses the preparation, characterization, and clarification of the growth mechanism of PbS, wires, ribbons, octapods (eight-arm stars), and hollowed cubes. These structures prepared by a thermal decomposition of a uni-precursor $\{[Pb(S_2CNEt_2)_2]_2\}$, using either en or ethylene glycol (eg) as an intermediate reagent, as well as surfactants. As will be discussed below, the obtained morphologies were governed primarily by the crystalline facets of the nucleating seeds. However, further crystal growth is controlled by the surface energy of the facets that were modulated by the solvent molecules. Also, a control of the growth regime, balancing between kinetic and thermodynamic growth, is determined by the variations in temperature and reaction duration. The synthesis of the PbS sub-micrometer structures, with dimensions ranging between 50 nm and a few micrometers, were based on the decomposition of a uni-precursor, lead-bis-diethyldithicarbamate $\{[Pb(S_2CNEt_2)_2]_2\}$, under a nucleaophilic attack of en or eg molecules at elevated temperatures.

II. Experimental Section

The preparation of the uni-precursor, $[Pb(S_2CNEt_2)_2]_2$, is described in detail in the Supporting Information. Then, two precursor solutions, consisting of 0.13 or 0.027 g of the uni-precursor, dissolved in 2 mL of en or eg, were prepared under standard inert conditions in a glove box, leading to pale yellow solutions. Separately, two different mother solutions were prepared, consisting of 8 mL of en or 6 mL of eg. The mother liquors were placed under a Shlenk vacuum line with a nitrogen flow and were heated to temperatures between 80 and 200 °C (considering the boiling point of en at 117 °C and that of eg at 195 °C). Then, 2 mL of each one of the uni-precursor solutions were injected rapidly into each of the two mother liquors, followed by a color change to black. Aliquots were drawn from the solutions every 5 min, over a period of 60 min. The produced PbS sub-micrometer structures were precipitated from the mother liquors by the addition of ethanol and centrifugation. It should be noted that the injection of the precursors into the mother solutions caused temperature reduction of about 5 °C.

The structural properties of the prepared structures were examined by high-resolution scanning and transmission electron microscopy (HR-SEM, HR-TEM). TEM observations were carried out on JEOL 2000FX instrument, operated at 200 kV. Images were recorded with Gatan MultiScan 791 CCD camera using the Gatan Micrograph 3.1 software package. Electron diffraction was recorded in selected area mode (SAED) using an aperture of 280 nm in diameter and camera length of 970 mm. The HR-SEM observations were carried out on a Zeiss Leo 982 instrument operated at 4 kV, including the measurement of energy dispersive analysis of X-ray (EDAX). The crystallographic structures were confirmed by the use of X-ray diffraction (XRD). Additional details regarding the XRD analyses are given in the Supporting Information.

III. Results

The syntheses discussed produced a variety of PbS sub-micrometer structures with varied dimensions and shapes, using uni-precursor molecules as the starting materials. These precursor molecules underwent a decomposition reaction upon a nucleophilic attack by the en or eg solvent molecules, as shown schematically in Scheme 1. This molecule consists of a Pb−S backbone and thione carbon bonds. On the basis of Scheme 1, we presume that the en or eg molecules attacked the thione carbon, as well as the Pb site, and then released the organic ligands shown in the scheme, accompanied by the formation of $[Pb_2S_2]$ dimers. The dimers eventually acted as reacting monomers in the sub-micrometer structures' growth. Alternatively, the nucleophilic attack at the Pb site produced $Pb(en)_2^{2+}$or $Pb(eg)_2^{2+}$ organometallic complexes (not shown) that were stable only at the lower temperatures; however, they decomposed rapidly upon a temperature increase close to the boiling point of the en or eg solvents. The use of the uni-precursor has the following merits: (a) balanced stoichiometric amounts; (b) simulta-

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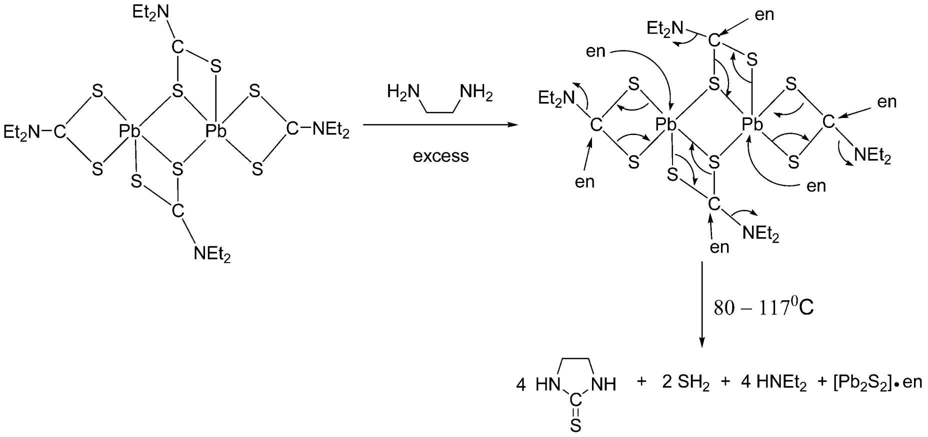
Scheme 1



neous injection of the ion sources; (c) several byproducts (e.g., organic residues of the uni-precursor); and (d) good control of the attachment and release of the surfactants of the various facets, permitting the growth of various shapes, by varying the temperature, solvents, and reaction duration (vide infra).

The XRD analyses of the wires, ribbons, octapods, and hollowed cubes produced, discussed subsequently, revealed that the various morphologies were comprised of a rock salt cubic structure with unit cell dimensions of 6.12 Å relevant to a rock salt structure with space group of $Fm\bar{3}m$ (see Supporting Information). In the following sections, the critical parameters that influenced the final morphologies of PbS sub-micrometer structures are discussed.

A. Role of the Solvent Molecules and Precursor Concentration. As indicated, PbS structures were synthesized in two different mother solutions, consisting either of en or eg molecules. The growth of the materials in en solution was carried out at a temperature range between 80 and 117 °C, while the growth in eg solution was carried out between 150 and 195 °C; temperature ranges were governed by restrictions regarding the boiling point of the solutions.

The growth in eg solution at 150 °C resulted in the formation of square plates and ribbons, with a typical thickness of 50 nm and an area of about 500 × 500 nm^2 for the square plates and about 200 × 700 nm^2 for the ribbons. Representative HR-SEM images, showing a top view of the plates and ribbons, are shown in panels A and B of Figure 1, respectively. An HR-SEM image of a side view is shown in Figure 1C. The squares were produced with a precursor solution of low concentration, while the ribbons were obtained with the highest precursor concentration. In fact, a closer look into the morphology of the ribbons (Figure 1D) suggests that the ribbons are comprised of an ordered assembly of the square plates, which diffused into one another.

The growth process in eg solution at 195 °C generated neither ribbons nor square plates but instead induced the formation of perfect cubes with typical size of 400 nm, shown by the HR-SEM image in Figure 1E.

The growth of PbS sub-micrometer structures in en solution produced completely different structures, starting from wires (discussed below) at the low-temperature range (80−100 °C), and continuing with the production of octapods and hollowed cubes at the high-temperature range (117 °C). Typical HR-SEM images of the high hierarchical structures are shown in Figure 2. Figure 2A and B represents octapod structures at different scaling, consisting of a central cube with eight branches merging away from the apexes. Each branch is composed of a stack of plates assembled along the branch axis and slightly slid with respect to one another. The SAED of those octapods (not shown) showed a polycrystalline nature. The described octapods described are not stable over a period of time (a few weeks) or upon an increase of the temperature. The hollowed cubes, shown in Figure 2C and D, developed gradually from the octapods by filling the space between the arms without further growth of the central cube. The cubes shown in Figure 2C have an

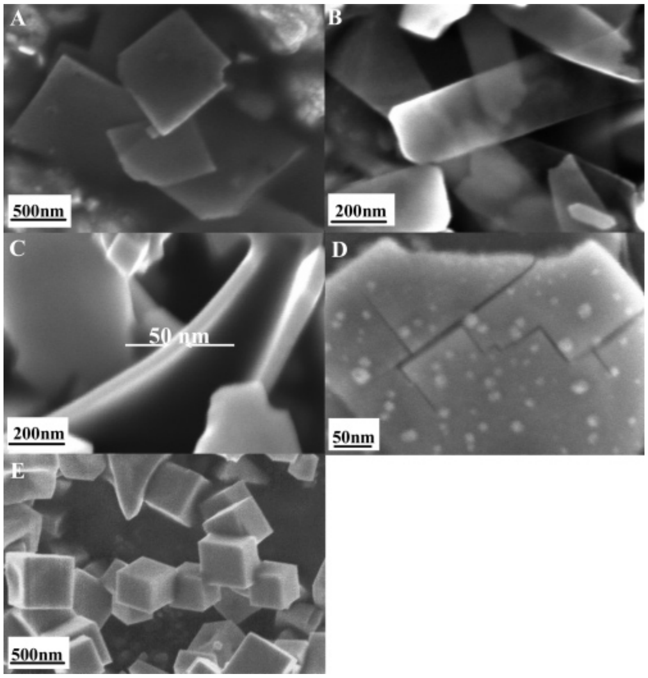


Figure 1. HR-SEM images of PbS square plates and ribbons with typical sizes of 500 × 500 (A) and 200 × 700 nm^2 (B), respecively, and a side view of the ribbons shown in (B) with a thickness of 50 nm (C); a magnified image of the ribbons is shown in (D). The ribbons and plates were prepared in eg solution at 150 °C. HR-SEM image of PbS full cubes produced at 195 °C in eg solution (E).

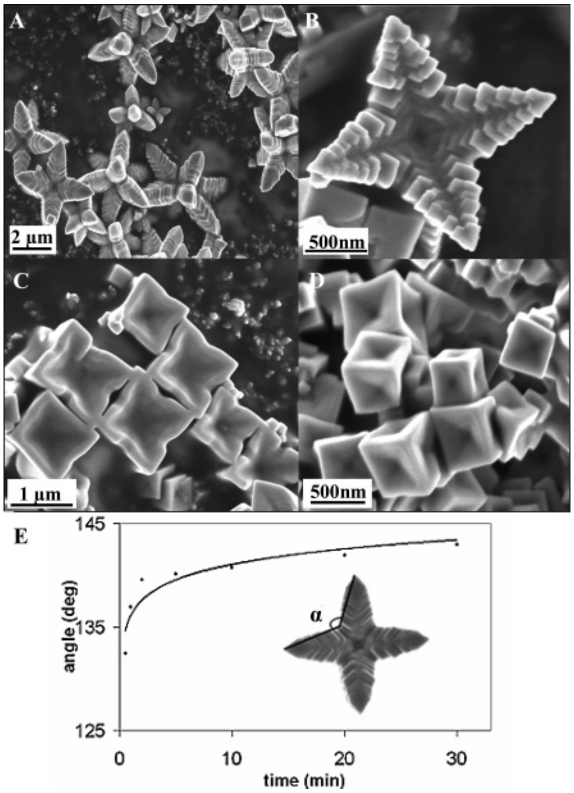


Figure 2. HR-SEM images of octapods, shown in different scales, produced in en solution with reaction duration at 10 min at 117 °C (A and B);. HR-SEM images of hollowed cubes produced in en solution at 117 °C, with a reaction duration of 20 (C) and 30 min (D); plot of the change in angle between the pods versus reaction time (E).

Table 1. Sub-micrometer Crystal Morphologies, Prepared by the Use of Different Solvents

shape	ethylene glycol	ethylene diamine
nanoribbons	yes	no
nanowire	no	yes
octapods	no	yes
hollowed cubes	yes	yes
full cubes	yes	yes
nanoplate	yes	no

~1 μm size and were drawn from the solution after 20 min, while the cubes in Figure 2D collapsed into a size of 500 nm after a reaction time of 30 min. Also, the structures shown in Figure 2D seem to already have a complete cubic circumference with negative growth toward the center.

It should be noted the octapods and the hollowed cubes were never observed during growth in eg solution and ribbons were never produced using en solutions. Table 1 summarizes the various shapes produced in eg and in en solutions, emphasizing the influence of the solvent molecules on the morphology of the sub-micrometer structures.

B. Role of the Duration of the Reaction. A change in the temperature and reaction duration enabled merging a preliminary morphology into a new structural form. For example, the octapods produced in en solution at 117 °C collapsed into hollowed cube structures (reducing the structure's size from a 2 μm octapod into a 0.5 μm cube) when the reaction duration time was increased, as shown in Figure 2. Figure 2E represents a plot of the change in the angle between the pods (marked in the inset of the figure) versus the reaction duration (minutes), suggesting recrystallization in the regime between the pods that finally form the hollowed cubes. This filling process between the pods nearly reaches a plateau after about 10 min.

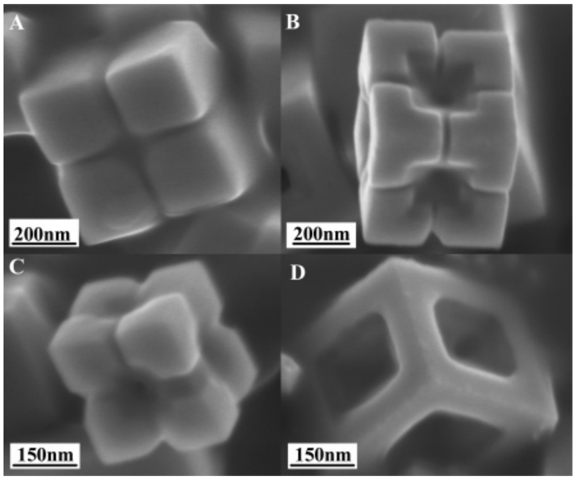


Figure 3. HR-SEM images of PbS sub-micrometer structures developed with the reaction, after 10 (A), 20 (B), 25 (C), and 30 min (D). Those cubes were grown in en solution at 117 °C.

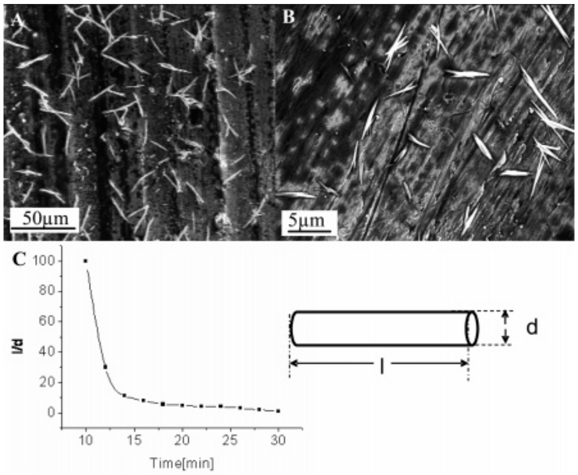


Figure 4. HR-SEM images of PbS wires produced in en solution at 80−100 °C, and were drawn from the reaction after 20 (A) or 30 min (B); plot of the aspect ratio (*l*/*d*, as defined in the inset of the figure) of the produced wires, versus the reaction time of a reaction produced at 100 °C.

Figure 3 presents the development of the hollowed cube over time, taking place in the en solution at 117 °C. The cubes produced after 10 min (Figure 3A) are composed of eight subcubes, an intermediate shape developed between the octapods and the forming cubes. As time develops, the frame of those subcubes effuse into one another (Figure 3B−D), to form a perfect circumference; however, the holes at the six {100} facets become larger and larger.

C. Role of the Reaction Temperature. The growth of PbS wires in en solution at relatively low temperatures showed the production of long, thin wires at the lowest temperatures (80−100 °C), as shown in Figure 4A. These wires became thicker and shorter with the extension of the reaction duration (Figure 4B). Additional HR-SEM images of the PbS wires are included in the Supporting Information. Figure 4C exhibits the dependence of the aspect ratio of the wires (length [*l*]/width [*d*]) on the reaction time. This plot suggests that the wires can be produced within the first 15 min of the reaction, while prolonging the reaction time converts the wires into full cubes, characterized by the small (l/d) ratio.

The temperature also influenced the crystal growth in eg solutions. As shown in Figure 1, the ribbons were produced primarily at 150 °C (50% efficiency) and they disappeared completely when the temperature was increased to 190 °C. At that temperature, perfect cubes with 100% efficiency were produced.

IV. Discussion

The formation of PbS sub-micrometer structures with various symmetries and shapes is determined by the *nucleation* and the subsequent *growth* stages. The growth process develops according to the *crystal habit* and to the *branching* process. A crystal habit is associated with the energy of the exposed facets, while the development of the branching is with associated a diffusion effect.

The initial factor responsible for the final shape of the structures is the crystallographic phase of the seed formed during the nucleation process. In general, this factor depends on the nature of the material and on the environmental conditions (e.g., temperature). However, it is known that a PbS semiconductor crystallizes as a rock salt structure at any temperature. Cheon et al. proposed that PbS seeds crystallize as tetradecahedrons (truncated cube), exposing six {100} faces and eight {111} faces.

The habit of a rock salt structure reveals that the {111} facet has a higher energy than that of the {100} due to higher packing density and the larger number of under-coordinated atoms. Actually, the growth kinetic energy barrier is inversely proportional to the surface energy, suggesting a faster growth rate along the <111> direction compared to the other directions. This leads to a consumption of the monomers by their adsorption on the most energetic facet. Such a process first of all directs the growth of branches and the formation of octapods, followed by the formation of hollowed and full cubes. Still, the creation of such symmetric structures depends on the following environmental parameters: (a) choice of stabilizing surfactants and their steric effects; (b) choice of the growth regime differentiating between thermodynamic and kinetic growth, determined by the temperature and reaction duration; and (c) requirement for a large concentration of the precursors to enable a fast kinetic growth and Ostwald ripening effect.

As mentioned, the en and eg solvents play a major role in the reaction. These solvents act as nucleophilic agents, attacking the Pb atoms of the precursors to form an intermediate organometallic complex (e.g., $\mathrm{Pb(en)_2}^{2+}$). As discussed in our previous publication, the $\mathrm{Pb(en)_2}^{2+}$ complex is stable up to ~100 °C with a trans configuration that inhibits crystalline growth parallel to the {111} surface, while permitting the growth along the <100> direction. Thus, a wirelike structure is formed between the temperatures of 80 and 100 °C, as shown in Figure 4. In contrast, upon a temperature increase to 117 °C, these wires collapse into a cube shape due to the decomposition of the $\mathrm{Pb(en)_2}^{2+}$ complex and a permission of a thermodynamic control process, governed by the habit of a rock salt structure. The growth of PbS crystals in eg solution, also initially formed a $\mathrm{Pb(eg)_2}^{2+}$ complex; however, it is known to be less stable than $\mathrm{Pb(en)_2}^{2+}$ and decomposes at 195 °C. Thus, the $\mathrm{Pb(eg)_2}^{2+}$ complexes are less effective in the screening of the {111} facet and a slower growth in this direction leads to the formation of the plates and ribbons. The ribbons and plates developed into full cubes upon the increase of the temperature, the reaction time, or the concentration of the precursors. These experimental changes shifted the growth from the kinetic into the thermodynamic regime.

So far, the discussion has presented the role of the en and eg solvents as intermediate agents in the reaction; however, at the elevated temperatures used (close to their boiling points), these molecules act as surfactants. Cheon et al. proposed that the amine molecules stabilize the {100} surfaces and, thus, enhance the natural habit of the rock salt structure to react faster along the <111> direction. This leads to a preferential kinetic growth of branches and the formation of the octapods when immersed in en solution at 117 °C. The branching growth, though, generates a large surface area with many dangling bonds and exposed {111} facets. This can rapidly increase the growth kinetic coefficient between the pods, while the {100} surfaces of the original tetradecahedron are still blocked by the amine surfactants. As the reaction proceeds, the multi-pod structures subsequently lose their shape (see Figure 2), accompanied by a preferential creation of the cube circumference and a formation of a hole at the central part of the cube. Those holes are formed due to a steady capping of the {100} facets by the en molecules. It should be noted that hollowed cubes are less pronounced in the growth of the structures in eg solution, due to the weaker binding of the eg to the {100} surface.

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Supporting Information Available: Experimental details and additional spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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