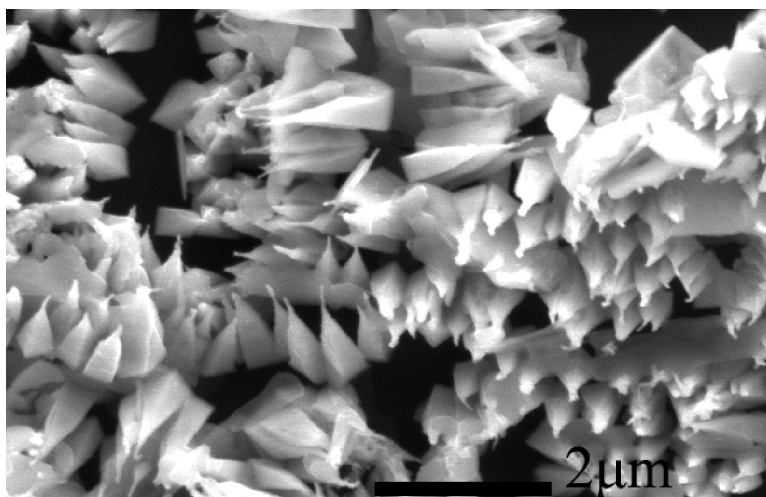Communication

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Pyramidal Lead Sulfide Crystallites With High Energy {113} Facets

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Lead sulfide (galena) has been known as a distinct entity since antiquity and was described by Pliny.[1] It is readily recognized in nature by its distinctive crystal habit as small cubes ({001} faceted) with the occasional occurrence of forms involving the expression of the (111) faces of the octahedron or tetrahedron and ready cleavage of the cubes along the (111) planes. The form of the crystal has attracted attention for well over 100 years.[2] After detailed calculations, Dowty[3] has ranked the stability of faces in the order {100}, {111}, {110}, {113}, {210} and noted that this is not perfect, especially as regards the form {113} which is never observed.[4] Indeed, to our knowledge, both natural and synthetic forms of PbS show only {100} or {111} facets.[2,5,6] In this letter, we report a simple method for the preparation of square based pyramids with {113} faces and {002} basal planes. These unique crystals have been formed by precipitation at the interface of toluene (lead containing) and water (sulfide containing) solutions. The form of the precipitate is remarkably dependent on reaction conditions. We believe that this route could make available materials in new forms with interesting properties[7] and provide further insight into classic problems of crystal growth.

PbS crystallites in the shape of pyramids are obtained as pale gray deposits at the interface between a toluene solution of lead diethyldithiocarbamate and an aqueous solution containing a slight stoichiometric excess of Na_2S at 50 °C over 2 h (Figure 1). The crystallites are pyramidal with a square base and four triangular faces. The pyramids are close to monodispersed and spontaneously form a monolayer consisting of upright pyramids in direct contact, principally at their bases, and spread across the entire water−toluene interface.

The dimensions of the pyramidal crystallites can be controlled by changing the reagent concentrations. The base length changed from 574 to 1259 nm as the concentration of the solution was increased from 0.56 to 1.67 mM (see supplementary images). In all cases, pyramidal crystallites were the only products, and the deposition was confined to the interface. The change in reagent concentrations does not affect the ability of pyramids to form monolayered films. The pyramids are always capped by thin wisps that presumably seed the growth. Notably, the aspect ratio of the various batches of pyramids (ratio of height to width) is constant at 2.12. Further, the angle between the edges of the triangular face and the square base is a constant at 66°.

X-ray diffraction patterns obtained from the monolayered films are characteristic of cubic PbS crystallites with the rock salt structure oriented along the (002) and (113) planes (Figure 2a). High resolution transmission electron microscopy suggests that the individual PbS pyramids are single crystals. Lattice fringes with spacing corresponding to the distance between the (002) planes of PbS are seen parallel to the base (Figure 2b,c) along the entire length of the pyramid. The wisps at the apex of the pyramids are frequently detached but show lattice fringes characteristic of PbS. Therefore, interfacial deposits consist of vertically oriented pyramids with the (002) basal plane parallel to the substrate and truncated with
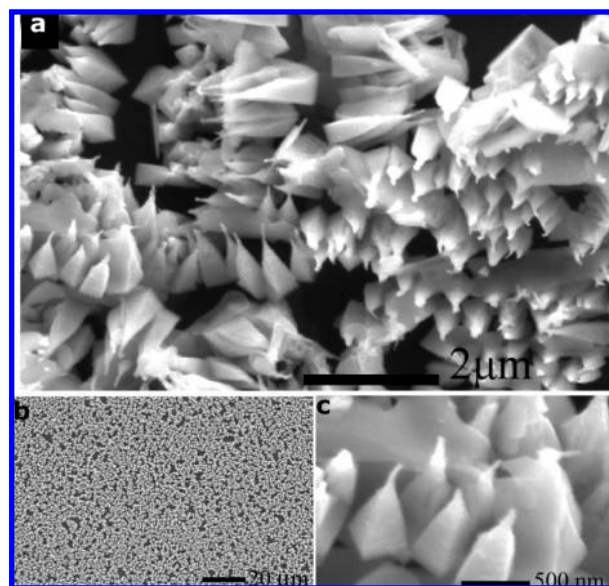

Figure 1. (a−c) SEM images of PbS pyramids obtained using 30 mL of 1.67 mM lead diethyldithiocarbamate in toluene and aqueous Na_2S (10% excess). The images in a and c correspond to films that were scratched to facilitate imaging of pyramids.

triangular faces along the (113), (1−13), (−1−13), (−113) planes (Figure 2d). The expected aspect ratio of such pyramids (ratio of lengths OL and MN, Figure 2d) is $3/\sqrt{2} = 2.12$, corresponding to the experimentally observed ratio, suggesting that the pyramids do adopt this unusual growth habit. Further, the observed interfacial angle (between the square base and the triangular face) is close to the expected angle ($\angle LMN$, Figure 2d) of 64.8°. The pyramids are slightly flattened and distorted close to the apex due to the change in the growth mode from the seeds (wisps) to pyramidal form.

The single most remarkable aspect of this study is the slow growth along [113] direction resulting in the pyramids with {113} facets. In crystals grown under slow (equilibrium) growth conditions, the facets binding the crystallites directly relate to the surface energies (γ) of the various facets.[5] Facets with low surface energies dominate the morphology as growth is slower along these directions. PbS has the simple rock salt (halite) structure, and studies of sodium chloride system are relevant to understanding this system. On the basis of experimental and theoretical studies, the surface energies of the various faces are expected to be in the order $\gamma_{100} < \gamma_{111} < \gamma_{110} < \gamma_{113} < \gamma_{210}$.[2,3,5,6] PbS crystallites therefore usually exhibit {100} facets, and under kinetic control, the relative growth rates of the different faces are altered to obtain {111} facets.[2,6] Higher energy surfaces such as {110} are rarely seen, as the conditions necessary to stabilize them and alter the relative growth rates are rather severe.
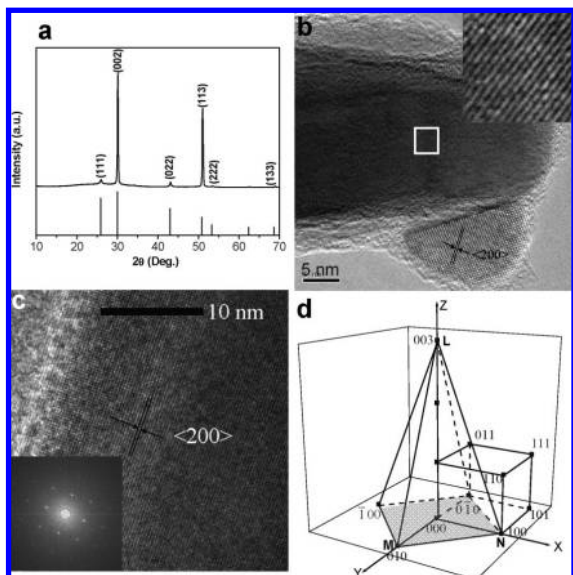
Figure 2. Structural characteristics of PbS pyramids. (a) Powder X-ray diffraction pattern obtained from as grown films. The expected positions and intensities of the standard peaks are indicated. (b) High resolution transmission electron microscopic (HRTEM) image of the tip of a PbS pyramid revealing (002) lattice planes throughout the imaged area. Inset shows a magnified view of the picture; (c) HRTEM image of base of a PbS pyramid. The inset is a Fourier transformed version of the image; (d) schematic diagram showing the structure of a pyramid and its relation to the halite unit cell.

It has hitherto been impossible to obtain PbS crystals with the even higher energy {113} facets in either natural or artificial forms. The difficulty of growing crystals along [113] has been noted in previous studies.[3,6] It is therefore remarkable that the shift in the relative growth rates necessary to change the growth habit to [113] can be achieved by means of a small temperature change in the present system. The ability to alter the growth habit at liquid−liquid interfaces is novel. We envisage that this method could be a powerful new addition to the techniques of crystal growth and is capable of producing high energy facets on numerous crystallites under fairly mild conditions.

The interface between two liquids such as water and toluene are not sharp. The two liquids mix to a limited extent around the interfacial region forming emulsive layers immediately above and below the original interface whose properties such as density are distinct from either liquid.[8,9] In these interfacial layers, diffusion is markedly slower.[8] The solutes and their disassociation products are present in concentrations that can be higher (or lower) than what would be expected on the basis of bulk partition coefficients. We suggest that within, this emulsive region, a small, spatially well-defined region with controlled supersaturation of ions exists and serves as a growth medium for the pyramids. The evolving nature of the medium throughout the deposition is to be emphasized; growth of particulates lowers interfacial tension promoting further mixing. The wisps at the apex are probably the initial products that facilitate subsequent anisotropic growth.

In addition to the unusual growth habit, a number of other properties of the pyramidal single crystals seem to be influenced by the nature and properties of the liquid−liquid interface. Crystals with cubic unit cells such as PbS tend to adopt isometric shapes such as cubes or octahedra, when grown slowly in near equilibrium growth conditions.[2,6] However, unlike crystals growing in bulk solutions which have six isotropic growth directions, crystals growing in the interfacial region have only three isotropic growth directions. The hemihedral form (of the isometric octahedron)
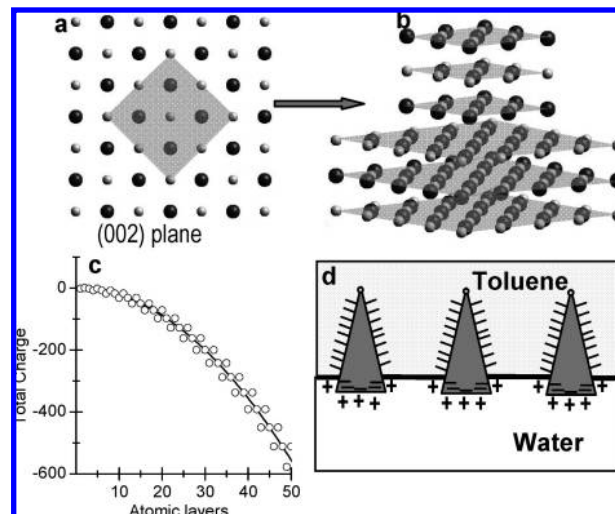

Figure 3. (a) Atomic layers that constitute the pyramid. S^{2-} ions are the larger spheres. The stacking sequence is shown in (b). (c) Plot of the charge naturally acquired by PbS pyramids growing as shown in (a). The calculation assumes the charges are not neutralized by adsorbents and ions. (d) Schematic representation of pyramids adsorbed at the water/toluene interface and asymmetric charging caused by the difference in dielectric constants between the liquids.

adopted by PbS crystallites is possibly a direct manifestation of this reduced symmetry in the growth medium.

Crystallites at fluid interfaces, such as the PbS in this case, need to adopt forms with high chemical potential in order to be adsorbed at the interface and form what is known as a Pickering emulsion. The chemical potential (or adsorption energies) of the particulates is dependent on the surface area of particles and the contact angle between particle surface, water, and toluene as well as the interfacial tension.[10] The adsorption energies of the PbS pyramids are of the order of 10^6 $k_B T$ per particle. The pyramids are thus strongly adsorbed at the interface. The chemical potential of adsorbed particles is further influenced by their surface charges.[10] The particles adsorbed at the interface are forced to charge asymmetrically, due to the difference in the dielectric constants of the liquids forming the interface. The PbS pyramids consist of square shaped {002} atomic layers, bounded by the (113), (1−13), (−1−13), and (−113) planes (Figure 3a). To satisfy the symmetry requirements of the rock salt structure, the atomic layers stack three times before the plane grows in size (Figure 3b). The individual layers making up the pyramidal crystallites are charged, as edge atoms can only be either S^{2-} or Pb^{2+} (Figure 3a). The stacking sequence prevents the structure from adopting a *per se* charge neutral form. In the absence of surface adsorbents, the pyramids possess substantial intrinsic charge (Figure 3c) and are naturally adept at charging asymmetrically due their shape. We believe these factors contribute to PbS adopting this unusual pyramidal morphology and perhaps explain why pyramids are the exclusive products of the interfacial reaction. In the reaction vessel, the magnitude of intrinsic surface charges may be reduced by the adsorption of liberated thiocarbamato ligands and/or binding of counterions (Figure 3d). Infrared spectra obtained from extensively washed samples of PbS pyramids reveal bands characteristic of the thiocarbamate group indicating that these ligands are sorbed on the surface of the pyramids.

Despite being strongly attached at the interface, the pyramids are free to move in the lateral direction to form tightly packed but unordered monolayers.[10,11] The pyramids acquire a dipole moment due to asymmetric charging. As the pyramids are all oriented in the same manner with respect to each other, there is a parallel
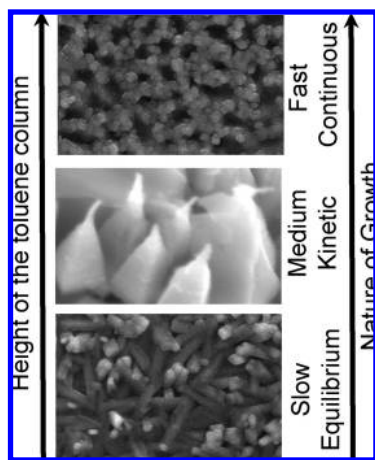
Figure 4. Illustration showing the influence of the height of the toluene column on the morphology of interfacial deposits as well as the nature of crystal growth at the water−toluene interface.

alignment of dipole moments leading to strong, long-range repulsion between the crystallites. If such long-range repulsive interactions dominate interparticle interactions, ordered mesostructures would result.[11] However, the tightly packed, unordered nature of the crystallites in the monolayers suggests that the long-range repulsion is effectively overcome by attractive forces. Capillary attraction caused by the particles distorting the shape of the surrounding meniscus could lead to strong, long attraction capable of overcoming dipolar repulsion if some residual charges are present in the toluene layer.[11] Additionally, van der Waals' interaction between the pyramids results in short-range attraction. We believe that the unordered monolayered films seen at the water−toluene interface are a result of capillary and van der Waals' forces overcoming the intrinsic dipolar repulsion between the crystallites.

Thus, the origins of this anisotropic growth as well as the self-assembly of the pyramids can be traced to factors at play in the immediate vicinity of the water−toluene interface. Previous work on interfacial deposition has primarily yielded spherical granules which are a characteristic of continuous growth under high supersaturation.[12] Simple changes to deposition parameters such as reagent concentration do not seem to be able to sufficiently alter the degree of supersaturation and thence the nature of products. Following systematic studies, we have identified a key factor capable of causing changes to the nature of crystal growth at the interface. We find that the height of the toluene column is crucial to determine the nature of interfacial deposits. Under conditions of constant reagent concentrations, growth time, interfacial area, and temperature, distinct changes in morphology occur on changing the height of the toluene layer. In cylindrical beakers with a 5.0 cm diameter, rods of PbS are obtained at heights of 0.5−1.0 cm, and pyramids, at heights of 1.3−1.7 cm, while even greater heights produce granular thin films (Figure 4 and Supporting Information). These observations are due to changes in growth kinetics mediated by solvo-dynamic factors. At low heights, reaction rates are lower and near equilibrium growth occurs, leading to the expected morphology, a two-dimensionally modified form (the rod shape) of the equilibrium 3D shape (cube). Higher growth rates (achieved by increasing the height of toluene column), lead to formation of kinetically controlled products, the pyramids. Indeed, further

increase in reaction rates by using the greater height of the toluene column or temperature leads to rapid deposition of granular thin films. Solvo-dynamic factors such as the height of the liquid column affect both the thickness of the stagnant emulsive layers and interparticle interactions and hence alter the nature of the deposits. The nature of the lead precursor can have a powerful effect on the characteristics of the deposits. For example, the use of the dibutyldithiocarbamato complex instead of the diethyldithiocarbamato gives thin films of spherical granules (see Supporting Information).

In addition to growing films of nanocrystals, the interfacial area has previously assembled particles from well-dispersed colloids.[13] These studies seek to tap into the dynamic nature of the interface to create less defect-prone self-assembled layers. This report significantly extends the scope of synthetic schemes involving fluid interfaces by demonstrating their ability to generate monodispersed anisotropic crystallites. Our understanding of shape effects on quantum confinement in nanostructures could be markedly improved by studying the electronic properties of these monodispersed pyramids. The slow growth process (taking place over a period of 2 h) could be subject to a variety of probes to further our understanding of crystal growth as well as the nature of forces between colloidal particles adsorbed at fluid interfaces.

Supporting Information Available: Images of PbS deposits obtained under different deposition conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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