Complex PbTe hopper (skeletal) crystals with high hierarchy†

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A facile and mild solution method has been discovered for the synthesis of complex PbTe hopper crystals in large quantities, which are highly similar to the cubic halite skeletal crystals formed from extreme supersaturation in salt lakes existing in nature. This route may provide a new approach to growing other complex semiconductor structures of high hierarchy.

Recently, there has been active research in the area exploring novel synthetic chemical methods for the synthesis of metallic[1] or semiconductor nanoparticles[2] with controllable sizes and shapes in the presence of a surfactant or a directing agent. The architectural control of nanoparticles with well-defined shapes is a key for the success of "bottom-up" approaches toward future nanodevice fabrication.[3] Recent advances have demonstrated that it is possible to control the growth processes of nanocrystals and their nanoarchitectures with complex forms and different compositions.[4,5] The presence of organic additives or surfactants,[6–9] self-assembled organic superstructures and templates with complex functionalization patterns[10] can direct the growth of inorganic crystals with controlled morphologies and architectures.[11] Recently, the electrochemically-controlled growth of a variety of Cu_2O crystals with different architectures has been reported.[12] Self-similar assembly of polyhedral mesophase crystals can produce hierarchical structures, as demonstrated by Liu *et al.*[13] Mesocrystals, formed in an intermediary stage in the presence of additives, have emerged as new kinds of superstructures with complex form.[14] However, synthetic inorganic crystals with complex form and high hierarchy prepared through a direct synthetic route without using any additives or the aid of other techniques have been rarely reported.

Lead chalcogenides are very promising materials for thermoelectric applications due to their narrow band gaps and face-centered cubic structure.[15] It was reported that PbTe and PbTe-based compounds are superior materials for solid state thermoelectric cooling and electrical power generation devices.[16] Thus, their synthesis has attracted intensive attention. Monodispersed PbTe nanocrystals,[17] hollow spheres and nanotubes[18] have been prepared in the presence of organic solvent. PbS dendrites can be grown in surfactant-assisted solution.[7,8] Recently, tetragonal $PbWO_4$ microcrystals with special hierarchical structures have been produced by controlling the solution reaction conditions.[9]

Natural cubic halite skeletal crystals formed from extreme supersaturation in salt lakes were first found many years ago.[19] However, such complex hopper crystals are rarely found for other functional materials. In this communication, we introduce a facile and mild solution method, without using any additives, for the synthesis of PbTe hopper crystals in large quantities by controlling the reaction conditions such as reaction time, concentration and temperature. The hopper PbTe crystals have rather high complexity and structural speciality.

Pure PbTe crystals can be easily grown by a hydrothermal reaction.‡ A typical XRD pattern of the product is shown in Fig. 1. All the peaks can be indexed to a face-centered cubic structure with the *Fm*3*m* space group (JCPDS, 38-1435). The composition analysis of the product was detected by XPS (ESI, Fig. S1†). The results showed that two different chemical environments for Pb and Te were found. The binding energy bands located at 137.0 and 571.7 eV correspond to Pb–Te, and the 138.1 eV band corresponds to Pb–O. The binding energy band at 575.6 eV corresponds to that for TeO_2.[20] The results suggested that the surface of the PbTe crystals could be partially oxidized due to exposure to air.

The SEM image in Fig. 2 shows that the majority of the product is composed of hopper cubes with a fascinating structure, accompanied by a small fraction of flower-shaped and tower-like crystals. The {100}, {110} faces are mostly exposed, corresponding to the strong diffraction peaks appeared in the XRD pattern. In contrast, the intensity of the {111} faces is very weak, but it is still observed. The edges of a hopper crystal extend outwards from its core with a tiny cubic center leaving step-like faces, *i.e.* a family of {100} between these edges. Such a hopper cube structure is very

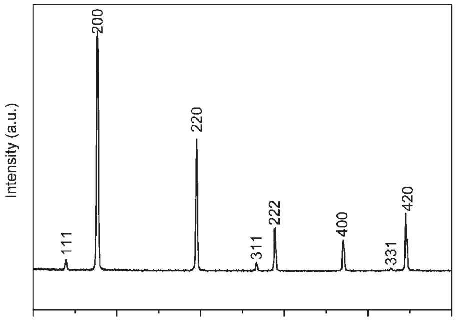

Fig. 1 XRD pattern of the PbTe product obtained by hydrothermal reaction at 160 °C for 24 h.

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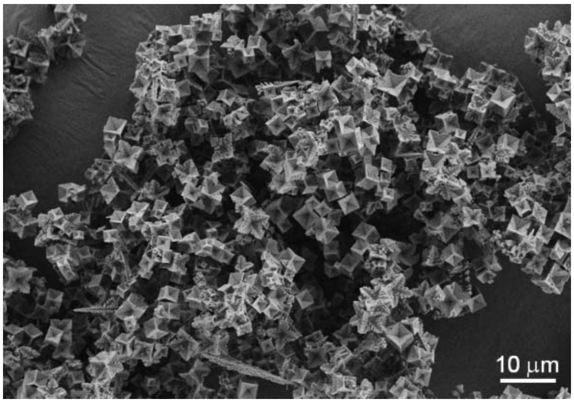


Fig. 2 SEM image of the hopper PbTe crystals synthesized by hydrothermal reaction at 160 °C for 24 h.

similar to that found in natural halite skeletal crystals formed from extreme supersaturation in salt lakes.[19]

When the time is extended to 4 d, flower-like crystals composed of eight identical tower-like horns are observed (Fig. 3). Surprisingly, we found that such hopper crystals (Fig. 4a) can further evolve into more complex forms with rather high complexity and structural speciality (Fig. 4b,c).

The results imply that the crystal growth mode follows a highly hierarchical path. The formation of the hopper structure has been found to be strongly dependent on the reaction conditions, such as reactant concentrations, reaction time and temperature. Here, the concentration is a key parameter. Decreasing the concentration of reactants to 10% (molar concentration) while keeping the KOH concentration the same does not produce any product. By keeping the concentration of reactants at 25% (molar concentration) in 4 M KOH solution, more tower-like crystals formed (ESI, Fig. S2†). However, when the amount of Na_2TeO_3 was increased to 1.25 mmol in 4 M KOH, more hopper crystals formed. (ESI, Fig. S3†). Flower-like crystals began to form if the amount of Na_2TeO_3 was increased to 2 mmol (ESI, Fig. S4†). Further increasing the amount of Na_2TeO_3 to 4 mmol resulted in the formation of more flower-like crystals (ESI, Fig. S5†). It must be pointed out that if the concentration of KOH is higher or lower than 4 M, the quality of the product is poor (data not shown here). Furthermore, temperatures that are too low, such as 90 °C, and reaction time that is too short are also not favorable for the formation of PbTe crystals.

Addition of surfactant (sodium dodecyl benzenesulfonate, SDBS) to the reaction results in the formation of more dendritic structures (ESI, Fig. S6†), underlying the fact that the surfactant can act as a capping agent, further increasing the surface energy differences between the {100} and {111} faces, as found in the formation of PbS rods.[5] The preferential absorption of molecules and ions in solution on different crystal faces directs the growth of nanoparticles into various shapes by controlling the growth rates along the different crystal axes.[21] Generally, the {111} surface intrinsically has a higher surface energy than do those of {100} and {110} faces for rock salt structures. The shape of a *fcc* nanocrystal is mainly determined by the ratio of the growth rate in the <100> direction to that in the <111> direction, faster growth on the {111} faces favors the formation of cube-shaped crystals.[1d,22] The formation of tetradecahedron seeds terminated by {100} and {111} faces has been observed previously in the case of PbS.[5] In present case, the formation of hopper crystals with mostly exposed {100} and {110} faces is due to the large differences between their growth rates and that for {111} faces. The prevailing growth rate for {111} faces will result in the diminishing of these faces, but more stable {100} and {110} faces will become mostly exposed under suitable hydrothermal conditions. Meanwhile, the adsorption and desorption of ions on the different faces of PbTe nuclei may kinetically favor the preferential crystal growth along a specific direction. The weak binding and differences in the binding

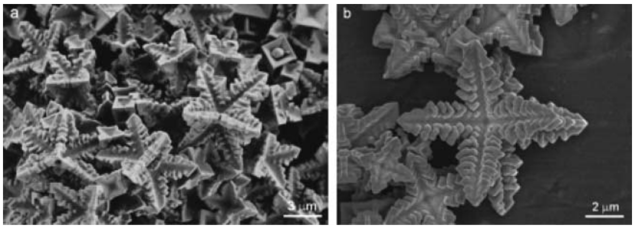


Fig. 3 Typical hopper crystals of complex morphology. (a) A general view of the crystals obtained after reaction for 96 h. (b) A magnified SEM image showing a typical crystal evolved from a cubic hopper crystal to form a complex and highly hierarchical structure made of 8 horns.

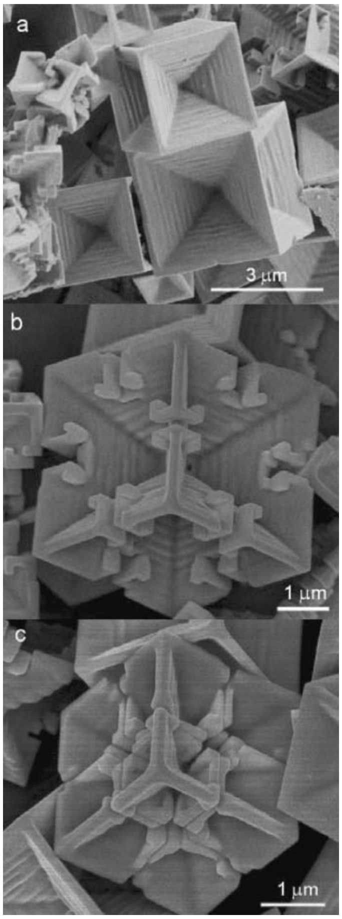
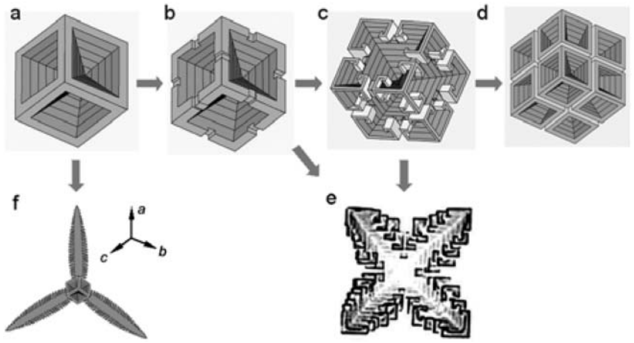


Fig. 4 SEM images of typical hopper crystals of complex morphology. (a) Hopper cubic crystals. (b) A hopper crystal starting to scroll in the center of each edge of the cube. (c) A complex hopper crystal composed of eight hopper crystals evolved from those shown in (a) and (b).



Scheme 1 Illustration of the hopper structures and their further evolution into more complex hierarchical structures.

ability of ions on the {100} and {111} faces will change the surface energy and shift the growth mode to the kinetic growth regime, resulting in preferential growth on the {100} faces and thus the formation of a minor fraction of tower-like structures (Fig. 2).

The shape evolution of PbTe crystals from hopper crystals with high hierarchy can be clearly identified, based on the series of experimental data summarized in Scheme 1. Hopper crystals are formed in the early stages (Scheme 1a) and then further evolve into the embryo state for highly hierarchical growth to form 6 × 2 gaps on the middle part of each edge (Scheme 1b). Then, the newly formed pair of edges of each gap, which are highly active, start growing towards the inside of the hollow space in parallel directions, tending to form new cubic corners and to close towards the inside (Scheme 1c). The newly formed edges shown in Scheme 1c join together to form a new kind of complex closed box, and finally form a complex hopper crystal composed of eight identical smaller hopper crystals (Scheme 1d). The repeated growth mode (Scheme 1c) of the newly exposed prismatic edge will lead to the formation of flower-like crystals (Scheme 1e). In addition, another highly hierarchical structure can be grown by preferential growth, starting from a hopper crystal, along its 3 of its prismatic edges that belong to 3 of its 8 corners (Scheme 1f).

In conclusion, we have demonstrated a simple hydrothermal synthesis of unique PbTe hopper (skeletal) crystals in large quantities without using any surfactants or capping agents. We also discovered a new highly hierarchical crystal growth mode that forms several kinds of fascinating rock salt PbTe superstructures with high complexity and structural speciality, suggesting that the hydrothermal approach can provide a versatile method for controlling the geometries and architectures of crystals with an unexpectedly high complexity and structural speciality. The flexibilities and capabilities of this approach are now being examined for other semiconductor materials.

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Notes and references

‡ In a typical procedure, analytically pure 5 mmol $Pb(NO_3)_2$ and 2.4 mmol Na_2TeO_3 were added to a 30 mL 4 M KOH solution. The mixture was stirred vigorously to form a homogeneous solution at room temperature. Then, 4.8 mmol KBH_4 was added and stirring continued for 5 min. The mixture was subsequently transferred into a 40 mL Teflon-lined stainless autoclave, which was sealed and heated at 160 °C for 24 h. The autoclave was then allowed to cool to room temperature. The gray precipitate was filtered and washed several times with distilled water and absolute ethanol to remove impurities. X-ray powder diffraction was carried out on the substrate using a Philips X'Pert Pro Super Diffractometer and Cu-K_α radiation (λ = 1.541874 Å). Scanning electron microscopy (SEM) images were scanned on the glass substrate using a JEOL JSM-6700F instrument. A FT-IR (MAGNA-IR 750, Nicolet Instrument Co., USA) was charged with dried powder from the solution. X-Ray photoelectron spectroscopy (XPS) was carried out on an ESCLAB M KII X-ray photoelectron spectrometer using Mg-K_α X-rays as the excitation source.

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