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Controlled synthesis of hyper-branched inorganic nanocrystals with rich three-dimensional structures

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Studies of crystal growth kinetics are tightly integrated with advances in the creation of new nanoscale inorganic building blocks and their functional assemblies[1-11]. Recent examples include the development of semiconductor nanorods which have potential uses in solar cells[12-17], and the discovery of a light driven process to create noble metal particles with sharp corners that can be used in plasmonics[18,19]. In the course of studying basic crystal growth kinetics we developed a process for preparing branched semiconductor nanocrystals such as tetrapods and inorganic dendrimers of precisely controlled generation[20,21]. Here we report the discovery of a crystal growth kinetics regime in which a new class of hyper-branched nanocrystals are formed. The shapes range from 'thorny balls', to tree-like ramified structures, to delicate 'spider net'-like particles. These intricate shapes depend crucially on a delicate balance of branching and extension. The multitudes of resulting shapes recall the diverse shapes of snowflakes[22]. The three dimensional nature of the branch points here, however, lead to even more complex arrangements than the two dimensionally branched structures observed in ice. These hyper-branched particles not only extend the available three-dimensional shapes in nanoparticle synthesis, but also provide a tool to study growth kinetics by carefully observing and modeling particle morphology. (203/180 words)

Hyperbranched nanocrystals are grown in the II-VI class of semiconductors, such as CdSe and CdTe, which have an intermediate fractional ionicity of bonds that poises them between two possible crystal structures. The basic branch point consists of a pyramidally shaped cubic zincblende unit with hexagonal wurtzite arms projecting outward at the tetrahedral angle. The branch is possible because the two crystal structures are close in energy and can occur at the same temperature and pressure (polytypism)[23,24]. Switching between the two structures can be driven kinetically; increased relative growth rate favors the cubic phase, while slower rates favor the hexagonal[24]. The preferential capping or stabilization by a surfactant of some crystal faces can change the kinetics and relative stability of crystal faces, a phenomenon also seen in the growth of snowflakes[25]. Organic stabilizers such as phosphonic acids are used to alter the crossover threshold, with higher phosphonic acid concentrations favoring branching at relatively lower concentrations of monomer and hence lower growth rate. Combinations of these parameters have previously been exploited to create tetrapods with controlled arm width and length[20] and to prepare dendrimer hetero-structures of generations one and two[21]. In the present work, we have shown the preparation of hyper-branched nanocrystals when these parameters are adjusted to more strongly favor branching conditions.

Hyperbranched nanocrystals were synthesized in a flask at elevated temperatures from a solution of metal ions in a mixture of tri-n-octyl-phosphine oxide (TOPO) and alkyl phosphonic acids[20,21] resulting in a batch of particles with similar morphology. Just like snowflakes[22], no two particles look exactly alike as their shape complexity increases, and yet particles of remarkably uniform character are obtained under a given set of conditions. We show representative examples for the variety of different shapes we can obtain in the transmission electron microscopy (TEM) images in Fig. 1. The different morphologies in the batches A to E are evident to the eye but difficult to quantify with a single parameter. However, simple parameters like particle diameter, "projected solidity" and the number of tips pointing outward on the two dimensional projection obtained from a statistical analysis of a large set of TEM images can be used to compare particles quantitatively. In the following sections, we describe the control parameters which can be varied to create these structures; the sequence of events that we infer to occur during

the growth process; and the application of TEM tomography to better visualize and understand these new hyper-branched materials.

One of the most important parameters that control the degree of branching is the concentration of the chalcogenide precursor. In the sequence of samples shown in Fig. 1a-c, the Cd precursor concentration is held fixed, and the total elapsed time is constant (20 minutes), while the Te precursor concentration is reduced progressively. The average particle total mass and the degree of branching, both increase significantly as the Te precursor concentration is decreased. These observations can be understood if the overall growth process is considered to occur in two steps: the initial formation of nuclei just after supersaturation and the subsequent process of growth of nuclei. At low Te concentration, relatively few nuclei form, so that the available monomer per nucleus during the growth phase is relatively high. This leads to fast growth (larger mass at 20 min.) and more branching (which is kinetically favored). At high Te concentration, many nuclei form so that the available monomer per nucleus during the growth phase is relatively low. This leads to slow growth (lower mass at 20 min.) and less branching.

Consistent with prior work,[13,14,16,20,21] we found that the quantity of the organic stabilizer and the chain length, play a key role in controlling the degree of branching and the morphology of the nanocrystals. Variation of the chain length of the stabilizer is particularly important, consistent with the view that the packing of the organic on the nanocrystal surface plays a role in stabilizing the zincblende structure (which is higher energy in the bulk) versus the wurtzite. Short chain phosphonic acids specifically increase the degree of branching. However, long chain phosphonic acids stabilize the wurtzite structure and therefore decrease the branching[13,20]. On the other hand, the reduction of the amount of phosphonic acids, while keeping the amount of Te fixed (0.117 mmole), increases the growth rate of the nanocrystal and therefore leads to thinner and longer arms[20]. These sparsely branched, delicate particles tend to align, with their almost 400 nm long and only 5-6 nm thick arms, forming large, intercalated networks. Their projected solidity is reduced to only 20% (Fig. 1d).

As part of this study, it was found that the choice of specific bi-functional organic groups versus mono-functional is also critical in promoting the fabrication of hyper-branched nanocrystals. The bi-functional groups may promote branching by creating new nucleation sites adjacent to an existing segment of nanocrystal surface, or because the local acid concentration is higher in the vicinity of any given binary surfactant compared to an equal number of independent acid groups on mono-functional surfactants. Some of the most interesting shapes were obtained using mixtures of a short chain bi-functional ligand [2-carboxyethylphosphonic acid (CEPA)] and the long chain tetradecylphosphonic acid (TDPA). A ratio of 1:11 of CEPA to TDPA, produced high yields of hyper-branched particles. Lower ratios (1:37) lead to very low branching while higher ratios (1:6.5) result in aggregation of spherical particles (Fig 2d-f). Control experiments with a mono-functional phosphonic acid such as propylphosphonic acid (PPA) instead of CEPA did not yield as high a degree of branching (Fig. 2a-c), while aggregation of nanocrystals was observed in the presence of even small amount of a di-phosphonic acid like ethyl diphosphonic acid (EDPA) due to the presence of two strong binding groups (Fig. 2g-i). CEPA combined the features of PPA and EDPA. Low concentration of CEPA promoted branching, with higher efficiency compared to PPA. High concentration of CEPA produced extensive aggregation, but with much lower cross-linking efficiency compared to EDPA (Fig. 2).

Substitution of Selenium (Se) for Te (Fig. 1e) changes the resulting morphology of the nanocrystals dramatically. The original tetrahedral symmetry is clearly visible, with multiple branches projecting outwards in groups from a single central tetrahedral branch point (Fig. 3b). The particles display high projected solidity (75 %) and a high number of projected tips on the outside (45) despite their relatively small size (200 nm) (Fig. 1).

TEM images obtained from aliquots taken at different time intervals from the same CdTe synthesis (using the base conditions defined above) suggest that the particles first grow four arms in a tetrapod-like configuration from which subsequently more and more branches evolve (Fig 3a). Branches seem to grow both from the center of the

particle and from the side of the outward growing arms. Interestingly, arms forming on the side of an arm point both forward and backwards with respect to the growth direction (Fig. 3a-upper left and Suppl. Fig. 1). This may occur when a twinned zincblende branch point forms at high growth rates.

The shape of the more compact particles produced are difficult to understand in the two-dimensional TEM image. In order to fully explore the rich three-dimensional structure of these particles, we performed scanning electron microscopy (SEM) and TEM tomography (Suppl. Fig. 1d). SEM allows quick and convenient observation of the surface structure for initial analysis and screening. TEM tomography allows for full three dimensional shape analysis. For TEM tomography, images of the same particle obtained at tilt angles from +/- 70 degree in 2-degree steps were aligned using 5 nm gold particles as markers. Examples for three tilt angles are shown in Suppl. Fig. 1a-c; a movie showing all tilt angles is available online). From the resulting stack of images, a full three-dimensional reconstruction is obtained (a side view is shown in Suppl. Fig. 1d). The particles observed in this way clearly show a main tetrahedral symmetry with one arm pointing straight up (masking it in the usual flat TEM projection). We observe contrast changes of the arms at different tilt angles characteristic for single crystalline materials (see movie, available online). This proves that each arm consists of a single crystal, which is sometimes bent in the case of the arms sitting on the surface. The detailed analysis of branch points shows both forward and backward branching (see images in Fig. 1-3) as well as points of multiple branching (e.g. Suppl. Fig. 1d, inset).

Similar to snowflakes[22], the hyper-branched CdTe and CdSe particles show a multitude of morphologies. Where conventional water snowflakes grow mostly in two dimensions[22], the CdTe and CdSe 'nano-snowflakes' grow in three dimensions starting from a tetrapod symmetry. We started to explore some and expect the discovery of many more distinct morphologies as the parameter space is further investigated. The detailed understanding of the growth kinetics should allow the tailored synthesis of particles with a desired three-dimensional shape beyond what we have already achieved. In addition, the particle morphology may serve as a test-ground for the theory of their growth.

Beyond these rationales, we think the awe-inspiring diversity of three-dimensional shapes of nano-snowflakes will delight many more scientists.

 (1507/1500 words)

Materials and Methods.

Cadmium oxide (CdO) 99.9%, 2-carboxyethyl phosphonic acid (CEPA) 94%, propylphosphonic acid (PPA) 95%, and tri-n-octyl phosphine oxide 99% (TOPO) were purchased from Sigma-Aldrich. N-tetradecylphosphonic acid (TDPA) 99% was purchased from PolyCarbon Industries, tri-n-octylphosphine (TOP) 97% from STREM Chemicals, Tellurium (Te) shots and 1,2 ethylene diphosphonic acid (EDPA) from Alfa Aesar and Selenium (Se) powder 99.9% from Aldrich.

Basic protocol for synthesis of hyperbranched CdTe or CdSe particles when the amount of Te or Se was 0.117 mmole.

CdO (0.15g, 1.1 mmole) was added in a mixture of TDPA (1 g, 3.59 mmole), CEPA (0.05 g, 0.32 mmole), and TOPO (3 g, 7.7 mmole), heated at 150 ˚C and kept under vacuum for 30 min to remove small amounts of water. Then the temperature was set at 335 ˚C and the brownish mixture was left under argon for 1 hour. This step resulted in a colorless solution due to the decomposition of the CdO and the formation of a Cd / phosphonic acid complex. TOP (1.2 g , 3.23 mmole) was injected and the temperature was adjusted to 335 ˚C. Te and Se stock solutions were prepared by dissolving Te or Se in TOP (5%, 3.1 % w/w, respectively). The mixture of Te:TOP (0.30 g, 0.117 mmole) or Se:TOP (0.30 g, 0.117 mmole) was injected into the hot reaction solution and the temperature was set to 330 ˚C (For all experiments the volume of the injected Te precursor was kept constant). The color changed from colorless to brownish within 4-5 minutes indicating the formation of nanocrystals. The solution was left at 330 ˚C for another 20 min before it was cooled down to 100 ˚C. Toluene (3 ml) was injected and the particles precipitated with isopropanol. To purify the particles from the reactants, the solution was centrifuged and the sediment re-dissolved in toluene. After a second precipitation with isopropanol, the sediment was re-dissolved in chloroform and kept for further analysis. Some particles settle down over time, but are easily re-suspended by sonication. The same procedure was followed to all the experiments by varying the tellurium/selenium or phosphonic acids concentration.

We would like to note, that our synthesis depends somewhat on the purity of the solvent used (TOPO)[26]. Especially the reaction kinetics seems to be affected by impurities[27] in the solvent, e.g. the total time to completion of the reaction as judged from a color change from colorless to black varies from 5 minutes to up to 10 minutes. Also, the morphology of the resulting particles varies slightly (Suppl. Fig. 2) using different batches and manufacturers of TOPO. It is, however, always possible to balance branching and extension with each batch of TOPO by slightly adjusting the phosphonic acids concentrations to produce particles with the desired morphology.

Figure 1. TEM images of hyper-branched particles grown under different reaction conditions. While the Cd precursor concentration was held fixed, the amount of Te was reduced progressively from 0.234 (a) to 0.186 (b) to 0.117 mmole (c), resulting in a: tetrapods with long arms (90 nm), b: Tetrapods with even longer arms (300 nm) and additional branching, c: hyper-branched particles with diameters around 550 nm. When the molar ratio of Cd to PA is lowered from 1:3.2 (as in a-c) to 1:1.6, very thin particles with average arm thickness around 6 nm resulted (d). Replacing Se for Te resulted in star-like particles shown in e. Scale bars are 100 nm (for the close-up images on the left), and 500 nm (for the overview images on the right), respectively. The diagrams in panel f-h show the average diameters, the projected solidity, and the number of tips on the particle perimeter as counted on the 2-dimensional TEM projection for the batches A-E as shown in panel a-e. The values are obtained from statistical analysis of at typically 50 images. The error-bar indicates the standard deviation.

Figure 2. Effect of mono- and bi-functional phosphonic acids on particle morphology. The ratio of TDPA to mono- or bi- functional phosphonic acid was varied from 37:1 (a,d,g), to 11:1 (b,e,h), to 6.5:1 (c,f,i). (a), (b), (c) mono-functional phosphonic acid; (d), (e), (f), bi-functional carboxyethyl phosphonic acid; (g), (h), (i) ethyl di-phosphonic. All scale bars are 100 nm.

Figure 3. Time evolution of branching observed by TEM images taken from aliquots collected at time intervals during the crystal growths for CdTe particles (a) and CdSe particles (b). Initially, the particles show a clear tetrahedral symmetry, which, as time progresses, is increasingly overgrown by additional branches. Whereas the CdTe particles (a) show branching off the initial arms (backwards and forward) as well as some arms forming from the particle center, the CdSe particles (b) grow arms mainly from the center or off the original arm. In the later case, the new arms seem to strongly align with the original arms retaining the original symmetry even for late stages of massive hyper-branched particles. Scale bars are 100 nm.

Supplemental Figure 1. Three-dimensional structure of the hyper-branched particles as obtained by TEM tomography (a-d) and SEM (e). For TEM tomography, images of the same particle are recorded at different tilt angles in 2-degree steps, e.g. 70 degree (a), 0 degree (b) and -62 degree (c) (scale bar is 100nm). The small dots are 5 nm gold particles used as alignment marks in order to create a well aligned stack of images, which is then transformed into a full, three-dimensional reconstruction. A side view of this reconstruction is shown in d, with a multiple branching point at the arm pointing upwards from the surface shown in detail in the inset.

Supplemental Figure 2. Effect of impurities in the solvent (TOPO) on particle shape. All experiments were done under the same reaction conditions according to the basic protocol. Different TOPO batch was used in each case. For the experiment (a) the TOPO was purchased from Sigma-Aldrich with 99% purity. For experiment (b) the TOPO was purchased from Alfa Aesar with 96% purity. For experiment (c) the TOPO was purchased from ACROS with 99% purity. For experiment (d) a different batch of TOPO was purchased from Sigma-Aldrich with 99% purity (different batch number than a).

Supplemental Figure 3. Effect of TDPA/CEPA ratio on particle shape. The TDPA/CEPA ratio was varied from 37:1 (a), over 11:1 (b) to 6.5:1 (c). A ratio of 37:1 leads to rods, bipods, tetrapods with long arms but no further branching (a). A ratio of

11:1 produces hyper-branched particles (b). A ratio of 6.5:1 resulted in aggregations of spherical particles with no specific shape. Scale bars are 100 nm.

Supplemental Figure 4. X-ray diffraction of CdSe and CdTe hyperbranched nanocrystals. The observed peak positions match those expected for the wurtzite phase for both materials. The 002 peaks are sharper than neighboring peaks which is consistent with crystalline domains elongated along the 002 direction.

Supplementary online information:

Movie of the aligned stack of TEM images of the same particle obtained for tilt angles between -70 and +70 degrees at every 2 degrees. The images were aligned using 5 nm gold particles as alignment marks. The movie shows a hyper-branched particle with four main arms, with three arms sitting on the surface and one arm pointing up. The contrast of the arms changes rapidly with tilt angles –characteristic of single crystalline material, proving that each arm is a single crystal. The arms near the surface are bend, which is indicated by the movement of dark areas with tilt angle.

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