Spray-Produced Coral-Shaped Assemblies of MnS Nanocrystal Clusters

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A novel spray-based technique enables the production of high-quality, free, uncoated semiconductor nanocrystals. Their collection, following spray droplet desolvation during flight, could result in unusual structures. We report on spray-produced ordered clusters (∼50 nm diameter) of MnS nanocrystals with grain size range of 1−2 nm and their assembly into micron-sized coral-shaped fractal aggregates. Ballistic cluster-particle aggregation, with the introduction of physical interaction between particles, is suggested as a model for the assemblies' growth.

Introduction

In the last two decades, significant attention has been devoted to the physics of low-dimensional semiconductor structures. Among those, semiconductor nanoparticles are of particular interest because of the pronounced influence of the three-dimensional size confinement on their electronic and optical properties.[1−6] Extensive efforts have been devoted to the production of high-quality semiconductor nanoparticles, motivated by their potential use in new and emerging technologies. However, the realization of technologically useful nanoparticle-based devices depends not only on the quality of the individual nanoparticles but also on their orientation and spatial arrangement. These nanoparticle assemblies may show tunable optical and electrical properties, which either preserve the individual nature of the nanoparticles or exhibit new collective effects.

Currently, there are two main methods for the fabrication of semiconductor nanoparticles, namely, epitaxial growth[7] and colloidal chemistry techniques.[8−11] Nanoparticles fabricated by epitaxial growth cannot be assembled. Colloidal synthesis procedures use organic passivating ligands which suppress attractive particle−particle interactions, prevent the formation of highly packed structures, and necessarily cause the arrays to be mechanically weak and often thermally and chemically unstable.

An attractive alternative to the conventional production methods is a novel spray-based technique for the formation and production of high-quality semiconductor nanocrystals (NCs).[12] According to this spray-based method, aqueous or organic solutions of semiconductor salts are first sprayed into monodispersed droplets, which subsequently become solid nanocrystals by solvent evaporation. The production of high-quality monodispersed CdS nanocrystals in the size range of 3−6 nm was demonstrated.[12] The spray-based method enables the production of free, uncoated semiconductor nanocrystals, in contrast to the colloidal method. Their collection one at a time, while particle−particle attractive interactions are not restrained (because of the absence of organic capping), results in unique and fascinating structures.

In this manuscript, we report on spray-produced ordered clusters (about 50 nm in diameter) of MnS nanocrystals in the grain size range of 1−2 nm and their assembly into micron-sized coral-shaped fractal aggregates.

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Experimental Section

Solution Preparation. Manganese sulfide powder (Aldrich) was dissolved in HPLC grade methanol. Mn concentration was measured via Spectra AA atomic absorption spectrometer (Varian Inc., Palo Alto, CA) equipped with standard air-acetylene burner system. A multielement hollow-cathode lamp, operated at the manufacturer's recommended conditions, was used at the primary Mn resonance line of 279.5 nm. The burner height and lamp position were adjusted for optimum sensitivity, and the nebulizer uptake rate was regulated to provide optimum absorbance signal for a conventional sample.

Spray System. Droplets of the manganese sulfide solution were generated using pneumatic-assisted thermospray. The pneumatic-assisted thermospray apparatus (shown in a figure in ref 12) employs a stainless steel capillary (127-μm ID, 510-μm OD, 20-cm long, Upchurch scientific), with liquid pumped through it by an HPLC pump (model PU-1585, JASCO, Japan) and through a polyetheretherketone (PEEK) tubing (65-μm ID, 1.6-mm OD). The PEEK tubing is connected to the stainless steel capillary by a PEEK union. A heating power supply is connected to two points on the capillary by specially designed clamps. The positive point is located near the inlet side and the negative point is located about 8 cm further downstream. The length between these connection points could be easily varied and served as an experimental parameter for varying the droplets' diameter. The capillary is then placed into a PEEK T-shaped structure to supply a nitrogen gas flow for pneumatic-assisted spray formation. The gas flows out of the T-shaped structure through a quartz tube surrounding the capillary. A kanthal wire is looped on the quartz tube for heating the nitrogen nebulizing gas.

Heating the air through which the spray passes on its way to the substrate target was achieved by using a small, axially open oven. The spray-produced manganese sulfide nanocrystal coral-shaped aggregates were collected on a variety of grids for transmission electron microscopy analysis (TEM) and high-resolution TEM analyses.

Manganese Sulfide Coral Assemblies' Characterization. High-resolution scanning electron microscopy (HRSEM) ob-

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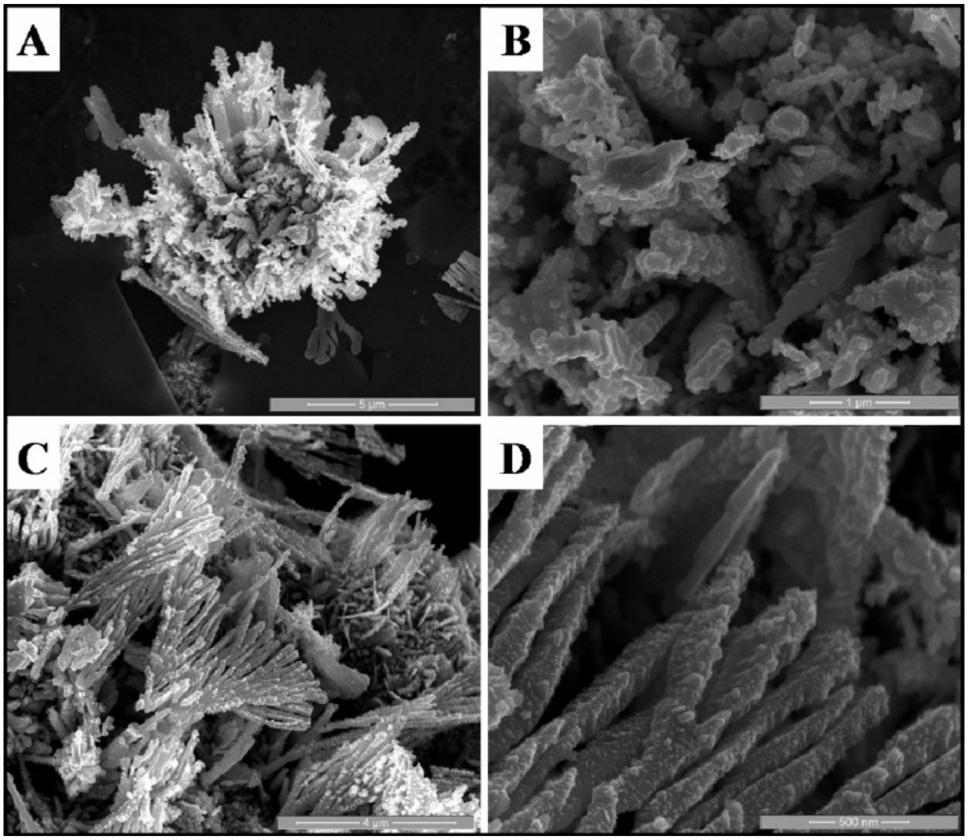

Figure 1. Spray-produced coral-shaped MnS assemblies. FEI Strata 400 Field Emission-SEM images of MnS micron-sized assemblies with the apparent shape of corals that were produced by pneumatically assisted thermospray. Images (A) and (C) demonstrate the resemblance to coral shapes. Images (B) and (D) are magnifications of images A and C, respectively, and illustrate the complexity of the structures.

servations were carried out on a Zeiss Leo 982 instrument operated at 4 kV and FEI Strata 400 Field Emission-SEM (Dual Beam system) operated at 10 kV. Transmission electron microscopy studies, combined with X-ray energy-dispersive spectroscopy (EDS) for elemental characterization and selected area electron diffraction (SAED) for structural characterization, were carried out on a JEOL 2000FX (TEM/STEM) instrument operated at 200 kV, a JEOL 3010UHR HRTEM instrument operated at 300 kV, and a FEI Tecnai F20 G^2 (S) TEM (equipped with energy-filtered imaging and high angular annular dark field detector for high-resolution STEM Z-contrast imaging).

Results and Discussion

Micron-sized MnS fractal assemblies with the shape of corals were produced by pneumatically assisted thermospray. Scanning electron microscopy images of two representative MnS assemblies are shown in Figure 1. Images A and C demonstrate resemblance to coral shapes. Images B and D are magnifications of images A and C, respectively, illustrating the complexity of these structures. Scanning transmission electron microscopy (STEM) images of the spray-produced MnS micron-sized assemblies (Figure 2) clearly demonstrate their fractal nature. Fractals often find potential applications as catalytic materials because of their relatively large surface area.[13] While the majority of the fractal assemblies have three-dimensional morphology (Figure 2A and B), a few have semi-two-dimensional morphology (Figure 2C and D) and grow perpendicular to the spray direction. This phenomenon should be taken into account when discussing the assemblies' growth models.

The generation of pneumatic-assisted thermospray droplets enables the controlled formation of monodispersed droplets with an average diameter in the range of a few microns, normally 1−3 μm. The primary droplet's size, when using stainless steel pneumatic-assisted thermospray system, depends on the percent of vaporization (thermospray control temperature), capillary internal and outer diameters, solvent characteristics (mostly volatile organics), and liquid flow rate. Median droplet diameters are shifted to smaller sizes as the control temperature or liquid flow rate increases as well as when the internal diameter of the vaporizer is decreased. Thermospray ability to produce relatively small droplets with narrow size distribution and the capability to tune their characteristic by the parameters indicated above have made it promising for the production of semiconductor nanocrystals.

While the spray-produced droplets are moving forward, at a certain point in time, the semiconductor salt concentration reaches the point of oversaturation because of solvent evaporation, and salt precipitation spontaneously occurs. Such spontaneous precipitation occurs within isolated droplets during their flight as unsupported isolated droplets, so that semiconductor nanocrystals can be produced, each from a single spray droplet. The average diameter and size distribution of a final spray-produced nanocrystal can be controlled and determined by the solute concentration of the sprayed solution and by the droplet size, hence by the spray production parameters, following the relationship:[14]

$$\frac{\text{droplet size}}{\sqrt[3]{\text{dilution factor}}} = \text{nanocrystal diameter}$$

MnS concentration in methanol was measured as 125 ppm. For this concentration, the single droplet to single nanocrystal process predicts the formation of nanocrystals of about 50−150 nm in diameter (for droplet diameters of 1−3 μm).

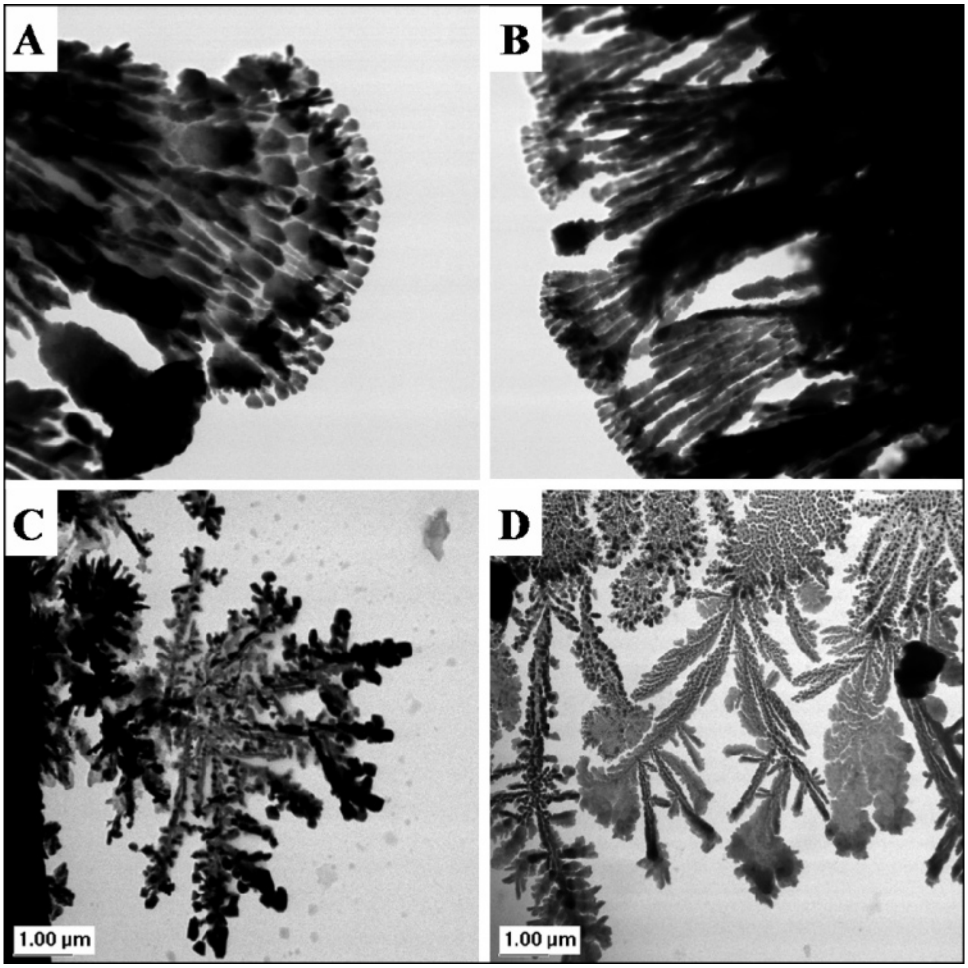

Figure 2. Spray-produced fractal MnS assemblies. Scanning transmission electron microscopy (STEM) images of the spray-produced micron-sized MnS assemblies which clearly demonstrate their fractal nature. Images (A) and (B) show the common three-dimensional fractal morphology. Images (C) and (D) show fractals with semi-two-dimensional morphology and growth direction perpendicular to that of the spray.

However, inspection of high-resolution TEM images of the coral-shaped assemblies, shown in Figure 3, reveals that the structures are composed of MnS nanocrystals in the size range of 1−2 nm, arranged in clusters with approximate diameter of 50−100 nm. This structure can only be explained by a multinucleation scenario. Accordingly, higher concentration levels within the solution could result in multinucleation sites in a single spray droplet, and consequently, upon solvent evaporation, a cluster of nanocrystals would be produced. These clusters represent a unique and novel higher hierarchy and are the building blocks of the micron-sized coral-shaped assemblies shown in Figures 1 and 2.

Figure 3 shows TEM images with various degrees of magnification of the clusters of MnS nanocrystals. Image A shows a fractal assembly. Its magnification, shown in image C, confirms that the structure is an assembly of clusters of MnS nanocrystals. This can also be seen in image D that was taken from a different structure. In image B, cluster assembly is clearly shown with an intermediate degree of magnification.

As corals in nature are colonial organisms and are composed of hundreds of thousands of individual animals called polyps, so also are the spray-produced coral-shaped structures composed of hundreds of thousands of individual MnS nanocrystals.

The assemblies are mechanically robust and retain their original structure for several months (as long as examined). This feature is particularly important for any future application of semiconductor nanocrystal assemblies and can be attributed to the lack of organic ligands.

A high-resolution TEM lattice image, shown in Figure 4A, indicates the high degree of crystallinity of the assemblies' structure. The formation of such highly packed structures is unique to the spray production method. Selected area electron diffractions (representative diffraction pattern in [011] orientation for β-MnS is shown in Figure 4B) indicate that the coral-shaped aggregates are made of the metastable phases, mostly β-MnS with a zinc blende structure and some γ-MnS with a wurtzite structure. A small fraction of the structures is occasionally made of MnS_2. Surprisingly, characteristics of single crystal diffractions were observed for the micron-sized coral-shaped assemblies. These unexpected results reveal the unique nature of these structures. For a single crystal diffraction to be obtained from an aggregate, all the nanocrystals composing that aggregate must be arranged with the same crystallographic orientation. This finding indicates an oriented attachment of a flying spray-produced cluster to the growing coral-shaped assembly. Furthermore, it implies that the nanocrystals composing such a cluster are ordered as well. This is striking, particularly when taking into account that a single 50-nm cluster is composed of thousands of nanocrystals and has less than 10 ms to form. In addition to the fundamental diffraction spots, superlattice reflections are observed in the pattern, indicating higher ordering. In the representative SAED shown in Figure 4B, three superlattice spots (indicated by the arrow) can be seen between the fundamental reflections in the 200 direction. This corresponds to a long period superlattice created by constant irregularity on each fourth layer (new long lattice parameter of

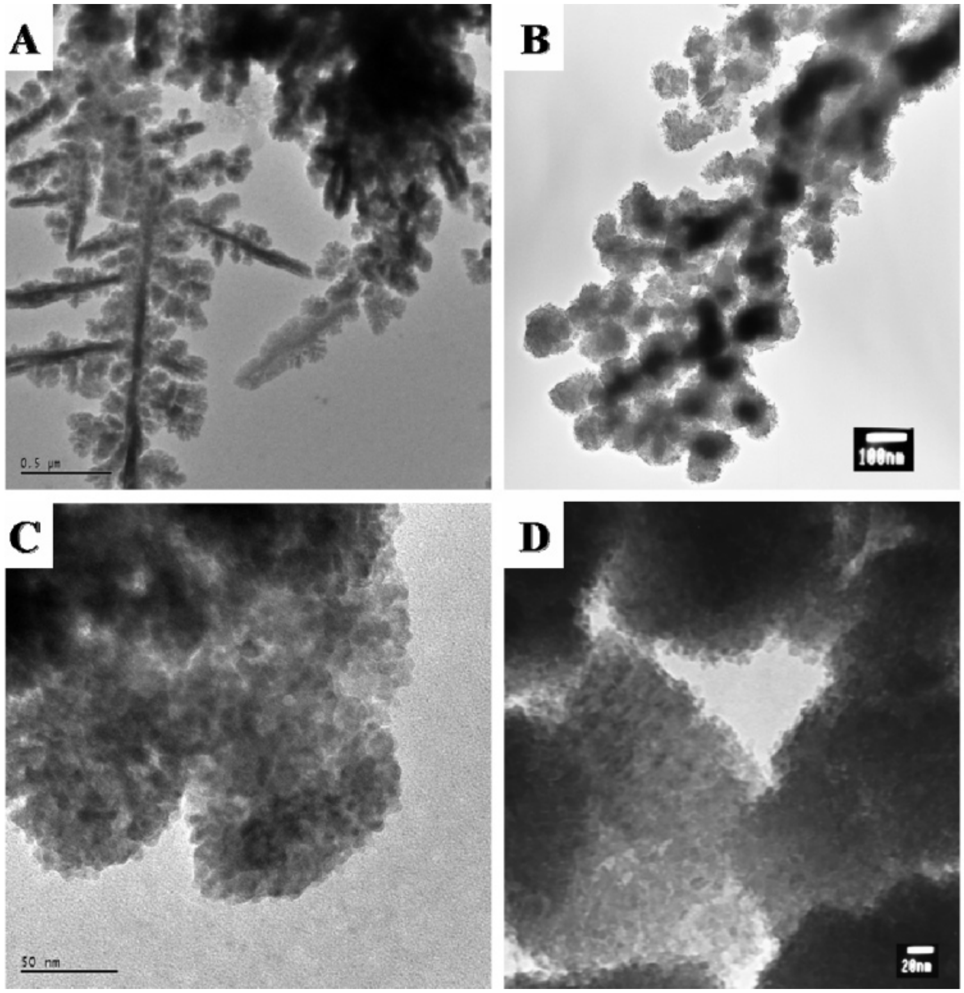

Figure 3. Clusters of MnS nanocrystals. TEM and HRTEM images of the coral-shaped assemblies reveal that the structures are composed of MnS nanocrystals in the size range of 1−2 nm, arranged in clusters. These clusters are shown with various degrees of magnification. (A) A fractal assembly. (C) The fractal magnification which confirms that the structure is an assembly of clusters of MnS nanocrystals. This can also be obtained from image (D) that was taken from a different structure. (B) Cluster assembly, clearly shown, with an intermediate degree of magnification.

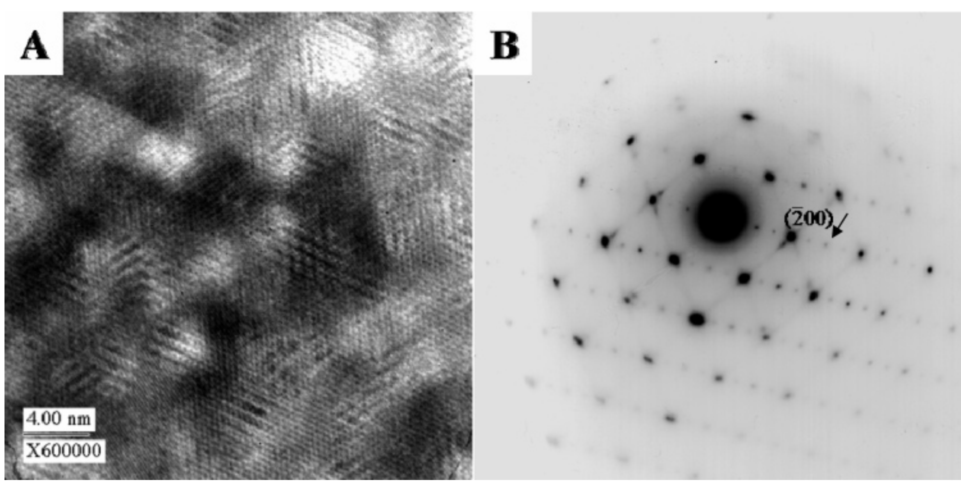

Figure 4. The ordered superstructure of the assemblies. (A) HRTEM lattice image showing the high degree of crystallinity of the structure. (B) A representative selected area electron diffraction (pattern in [011] orientation) that reveals an ordered superstructure of the coral-shaped assemblies, with metastable phase β-MnS.

11.2 Å), which might be attributed to the nanocrystal surface (grain boundary).

X-ray energy-dispersive elemental analysis revealed an extra amount of sulfur (beyond the stoichiometry). The excess sulfur, whether in an amorphous phase in the void between nanocrystals or as an ordered lattice plane, might play a role in the formation of the coral-shaped aggregates, acting as “glue”. The origin of the extra amount of sulfur is still undetermined.

The coral-shaped MnS assemblies appear to be connected to the Cu grid and are formed on the grid with or without the presence of the supporting amorphous carbon film. However, the coral-shaped MnS assemblies were not obtained from sprays collected on nylon grids or metals such as Ni, Al, and Au. Consequently, it was inferred that the copper reacts with the spray product, probably forming Cu_2S. This reaction produces the Cu_2S seed that induces the initiation of the growth of the assemblies. This conjecture is further supported by the fact that the structure of Cu_2S closely resembles that of β-MnS. Such selective formation of the structures on copper may be used in future applications where specific growth locations would be desired.

As shown, fractal assemblies with coral shape were produced. The formation mechanism of these assemblies requires attention and discussion. The size of these aggregates far exceeds the range of forces holding them together. Thus, it seems likely that the aggregation process can be understood without reference to the details of these forces.

In recent years, much interest has focused on nonequilibrium aggregation processes, that is, the formation of structures by irreversible addition of subunits. A successful model for such a process was developed by Vold and Sutherland.[15−16] In this model, known as ballistic aggregation, particles which are moving in straight lines are added to a structure whenever they touch a previously added particle.

In cluster-particle aggregation, particle trajectory plays a crucial role.[17] It is the trajectory that prevents particles from penetrating into the open structure of the fractal aggregates to form a denser structure with a higher dimensionality. Linear trajectories ($D_t = 1.0$) with randomly chosen directions lead to compact structures characteristic of ballistic aggregation.[18] However, the trajectories of particles in most natural growth processes are subject to deterministic, interaction-induced influences in addition to more or less severe stochastic perturbations. Introducing a physical interaction between the particle and the growing cluster means that tenuous fractals may be grown via deterministic, linear trajectories, which have preferential directions.[19] For example, in the presence of short-range attractive forces among the particles, the straight-line trajectories of the ballistic aggregation model would curve.[20]

According to the above discussion, we suggest that the coral-shaped assemblies were produced according to ballistic cluster-particle aggregation with the introduction of physical interaction between the particles. A cluster, which results from a single droplet, flies in a straight line from the direction of the capillary outlet toward the grid. When approaching close proximity with the growing aggregate, attractive forces curve the trajectories, enabling three-dimensional (3D) growth to a wide variety of directions. Without the introduction of physical interactions, growth direction perpendicular to the spray, such as the one seen in Figure 2C and D, could not be obtained with a ballistic aggregation model. Furthermore, the coral-shaped assemblies demonstrate a “fan” shape (Figure 2) which is a known result of ballistic aggregation formed by attachment to a seed,[16,21] probably the Cu_2S seed discussed above.

Conclusions

With currently available production methods, the fabrication of highly packed, robust assemblies of nanocrystals, which are essential for future applications, is hard to obtain. An attractive alternative to conventional production methods is offered by a novel spray-based technique for the production of high-quality semiconductor nanocrystals. The method uniquely enables the production of free, uncoated semiconductor nanocrystals. Collecting them during their flight, while attractive particle−particle interactions are not restrained (because of the absence of organic capping), results in unique and fascinating assemblies of nanocrystals. In this paper, we presented an example for such structures and reported on spray-produced ordered MnS nanocrystal clusters and their assembly into micron-sized aggregates with the shape of corals. A model of ballistic cluster-particle aggregation with the introducing of physical interaction between the particles was suggested for the coral-shaped assemblies' growth.

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