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General Synthesis of Uniform Metal Sulfide Colloidal Particles via Autocatalytic Surface Growth: A Self-Correcting System

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After decomposition of thiourea (TU) in the presence of various metal cations to form metal sulfide nanoclusters, an autocatalytic reaction between TU and the surface of the as-formed metal sulfide dominates the further growth of these metal sulfide nanoclusters. This autocatalytic surface growth is self-correcting, leading to formation of uniform metal sulfide colloidal particles. The size (from nanometer to micrometer) and shape of the particles are able to be tuned simply by varying the reactant concentration, reaction time, and temperature. More complex anisotropic particles can also be prepared in the autocatalytic surface growth system.

Introduction

Colloidal particles have been fabricated and engineered as the building blocks of advanced materials with ever renewable applications.[1−12] Among the colloidal particles, those formed by metal sulfides show unique semiconducting properties,[14] and they have been widely used in fields[3,12−16]

such as catalysis, opto/thermal-electronic device fabrication, photonics, and chemical sensing or detection. Organometallic and related synthetic methods have been demonstrated to be effective for the formation of highly uniform metal sulfide nanoparticles (smaller than 30 nm).[4,6−8,16−19] However, usually the as-obtained products are hydrophobic, and the reaction temperature are high, whereas applications of colloidal particles in catalysis, biochemistry, and device fabrication require the particles to be water-dispersible.[16−21] Moreover, through the current mainstream synthetic methods, the size of the obtained colloidal particles usually diverges immediately after the uniform particles are formed.

Autocatalytic surface growth, which was confirmed in the process of preparing Ir(0) nanoclusters with hydrogen as reductant,[22] has been adopted for the synthesis of larger nanoparticles with smaller ones as "seeds". Unlike the mainstream organometallic and related synthetic methods, the typical feature of which is the rapid and separate two-stage precipitation including a short nucleation burst in a supersaturated solution and the growth of the nuclei at an elevated temperature, the autocatalytic surface growth is a

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Table 1. Reaction Parameters for the Preparation of Various Metal Sulfide Colloidal Particles

sample	metal source/(M)	TU/(M)	PVP/(M)	temperature/(°C)	time/(h)
ZnS-Figure *3*A	$Zn(NO_3)_2 \cdot 6H_2O$/0.1	0.1	0.1	140	24
ZnS-Figure *3*B	$ZnSO_4 \cdot 7H_2O$/0.1	0.1	0.1	100	24
CdS-Figure *3*C	$Cd(NO_3)_2 \cdot 4H_2O$/0.1	0.1	0.5	140	8
$Cd_{0.8}Zn_{0.2}S$-Figure *3*D	$Cd(NO_3)_2 \cdot 4H_2O$/0.08 $Zn(NO_3)_2 \cdot 6H_2O$/0.02	0.1	0.2	140	8
PbS-Figure *3*E	$Pb(NO_3)_2$/0.01	0.01	0.2	120	4
Ag_2S-Figure *3*F	$AgNO_3)_2$/0.05	0.025	0.1	30	8
Eu_2O_2S-Figure *3*G	$Eu(NO_3)_3 \cdot 6H_2O$/0.05	0.075	0.1	160	4

slow and continuous process in a mild system. Although autocatalytic surface growth has been widely accepted, direct experimental observations of such growth processes have seldom been reported.[22−24] We have previously demonstrated that the decomposition of thiourea (TU), which is stable up to 180 °C in reaction systems without metal cations, could be triggered by Cd^{2+} in a polyol system at a temperature far lower than 180 °C.[25] The nucleation process of CdS colloidal spheres was investigated, but the further growth of the as-formed colloidal spheres has not been fully elucidated yet. In this paper, we describe the autocatalytic behavior for the further growth of metal sulfide colloid particles in a mild reaction system. It is the reaction between TU and metal cations on the surface of the as-formed metal sulfide "seeds" (rather than the reaction between TU and metal cations in the mother solution) that dominates the further growth of the metal sulfide colloidal particles. More importantly, this synthetic system has been proved to be self-correcting, that is, the size distribution of the colloids becomes narrower with reaction time.

This surface growth approach is general and highly compatible for the synthesis of uniform colloidal particles of various metal sulfides without a size-selective process. All reagents needed in the synthetic system are common and commercially available, and no complex or critically controlled processes are involved so that the synthesis of uniform metal sulfide colloidal particles can be scaled up conveniently. In the synthesis, ethylene glycol (EG)—the only organic solvent with a high boiling point (ca. 198 °C) and a low saturation vapor pressure—is heated at a temperature below the boiling point in an airtight system, and therefore no gaseous species such as H_2S are exuded. Furthermore, via a surface growth mechanism, more complex nano/microstructures of metal sulfides can be obtained by finely tuning the reaction parameters. The as-synthesized products are all hydrophilic and can be dispersed in water and other common polar solvents to form stable colloidal solutions, laying the foundation for widespread applications of the colloidal particles.

Experimental Section

Materials. Polyvinyl pyrrolidone (PVP K30, MW = 58000) was purchased from BASF. All other reagents were of analytic grade from Beijing Chemical Factory and used as received. Deionized, high purity water (PURELAB Plus, PALL) with a resistivity of 18 MΩ cm was used throughout.

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Synthesis of Anisotropic CdS Colloidal Particles. A 1.080 g quantity (3.5 mmol) of $Cd(NO_3)_2 \cdot 3H_2O$, 0.266 g (3.5 mmol) of TU, and 0.777 g (7 mmol, calculated in terms of the repeating unit C_6H_9NO FW=111) of PVP were dissolved in 35 mL of ethylene glycol and stirred vigorously until homogeneous. The mixture was sealed in a 50 mL PTFE-lined stainless steel autoclave and heated at 140 °C for 24 h followed by cooling to room temperature. The as-formed colloidal solution was used as the seed for the preparation of anisotropic CdS colloidal particles. The mixed homogeneous solution, including one third of the as-formed colloidal solution, 0.72 g (2.33 mmol) of $Cd(NO_3)_2 \cdot 3H_2O$, 0.177 g (2.33 mmol) of TU, and 0.518 g (4.67 mmol) of PVP, and 23.3 mL of ethylene glycol, was further heated at 140 °C for another 24 h. The resulting product was separated by centrifugation with the help of acetone and washed thoroughly with deionized water and ethanol.

Typical Synthesis of Metal Sulfide Colloidal Particles. A certain amount of a metal salt, TU, and PVP was dissolved in ethylene glycol (35 mL) and stirred vigorously until homogeneous. The mixture was sealed in a 50 mL PTFE-lined stainless steel autoclave and heated for 4−24 h. The resulting product was separated by centrifugation with the help of acetone and washed thoroughly with deionized water and ethanol. The detailed reaction conditions are listed in Table 1.

General Characterization. The scanning electron microscopic (SEM) images were taken with a JEOL JSM 6700F electron microscope, while the transmission electron microscopic (TEM) and high-resolution transmission electron microscopic (HRTEM) images, and the energy-dispersive spectroscopy (EDS) were performed on a JEOL JEM-3010 TEM microscope equipped with an X-ray energy-dispersive spectroscopy system. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The optical absorption and photoluminescence (PL) spectra of Eu_2O_2S colloidal particles were recorded on a Perkin-Elmer L55 luminescence spectrometer.

Results and Discussion

Evidence for Autocatalytic Surface Growth. To reveal the further growth process of the metal sulfide colloids, we used the 370 nm CdS colloidal spheres (obtained at a temperature of 140 °C) as "seeds" to prepare larger particles. When treated in the same synthetic system with prolonged reaction time, the 370 nm CdS colloidal spheres just grew into larger uniform spheres slowly and continuously without the formation of new particles.

When using the same CdS colloidal spheres obtained at 140 °C as "seeds", we prepared uniform anisotropic colloidal particles in a similar synthetic system at a temperature of 100 °C as shown in Figure 1A−C. The unique anisotropic structure, with one sphere at submicrometer scale and the other at nanometer scale, confirms the surface-induced growth mechanism in our synthetic system. The growth of colloidal particles via solution routes are believed to be a
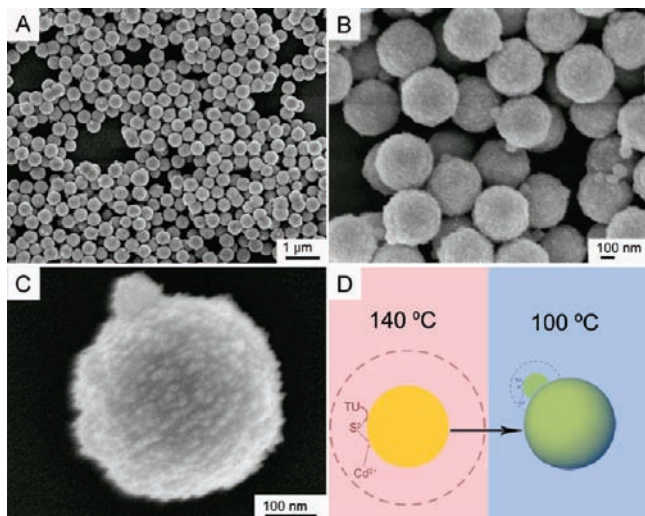
Figure 1. SEM images (A−C) and schematic representation of the formation mechanism (D) of CdS anisotropic colloidal particles.

diffusion-controlled process, that is, each particle nucleates and grows in one limited diffusion-controlled domain, as originally described by LaMer et al.[26,27] In general, according to the Stokes−Einstein equation

$$D = \frac{kT}{6\pi\eta r} \qquad (1)$$

where D is the diffusion coefficient, k the Boltzmann constant, T the reaction temperature, η the viscosity of the solution, and r the effective hydrodynamic radius of the spherical particles or molecules; the higher the temperature, the larger the diffusion-controlled domain of the system with other parameters being identical. Therefore, as shown in Figure 1D, when the larger CdS spheres obtained at a higher temperature are dispersed in a low temperature reaction system, the size of the "seed" does not match (maybe larger than) the diffusion-controlled domain, in which newly formed CdS clusters are confined. As a result, these CdS clusters can only attach to a part of the surface of the large CdS sphere to form a smaller CdS sphere, resulting in the anisotropic structure. It is the surface-induced growth that drives these CdS clusters to attach to the surface of the "seed" rather than to nucleate separately to form additional colloidal spheres.

It is worth noting that the metal sulfide is just a catalytic surface which accelerates the reaction between TU and metal cations. In the absence of metal cations, TU molecules remain stable in the colloidal solution of metal sulfide particles in ethylene glycol. Therefore, the whole growth process of metal sulfide colloidal particles can be separated into two stages: slow and continuous nucleation and faster autocatalytic surface growth. The time-resolved volume variation of CdS colloids (Figure 2A) is in good agreement with this growth process. The success in the preparation of uniform anisotropic colloidal particles conveys rather important information. On one hand, it demonstrates that not only
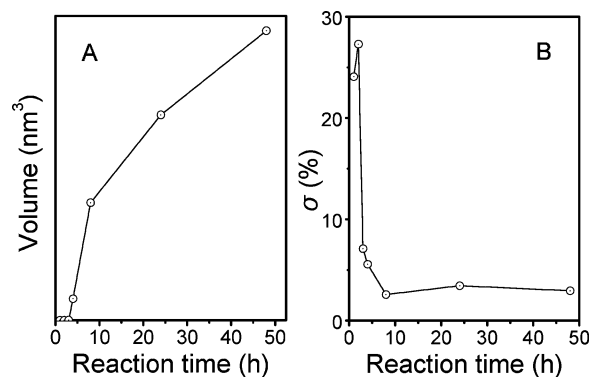
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Figure 2. Time-resolved volume variation of CdS colloids (A) and corresponding standard deviation σ values (B) (TU, Cd^{2+}, PVP: 1 M, 140 °C).

monodisperse colloidal particles but also more complex 3D structures can be obtained in a similar synthetic system. Whereas on the other, it reveals that the metal sulfide colloids indeed act as the catalytic surface for the reaction between TU and the metal cations.

Self-Correcting Growth. One of the limitations of conventional solution phase synthetic routes, such as the organometallic and related methods, and the sol−gel approaches is that the size distribution of the product usually remains narrow in a rather short period and becomes quite broad afterward. It is interesting that in our autocatalytic surface growth system the broad size distribution of the particles at the early stage of the whole growth process can be self-corrected at the following stages, and the size distribution after the self-correcting process remains highly narrow for a long time.

From Figure 2B, we see that the standard deviation (σ, calculated from the measured diameters of CdS particles using the computer program Microcal Origin, detailed results are shown in Supporting Information, Figure S1) of the size of CdS colloid particles is as high as 24% and 27.1% at 1 and 2 h, respectively. At the early stage of the growth process, the broad size distribution arises from the aggregation of as-formed primary nanoparticles into clusters. When the reaction time is prolonged to 3 h, the effect of self-corrected growth in this synthetic system becomes obvious, and the corresponding σ value decreases to 7.1%. Afterward, the size distribution becomes even narrower when the size increases gradually. The σ value further decreases from 5.6% (for 4 h) to 3.4% (for 24 h) and 2.9% (for 48 h). The unusual self-correcting phenomenon, which has never been reported before, is an important feature for our synthetic system.

After the autocatalytic surface growth mechanism is established, we can easily understand this self-correcting phenomenon. At the early stage of the particle growth, the rather broad size distribution is attributed to the temporary temperature gradient during the reaction temperature increase process, the newly formed nanoclusters, and the aggregation of the as-formed nanoclusters. After all the as-formed nanoclusters are aggregated, the whole synthetic system becomes homogeneous, and the amount of reactants for the growth of each colloidal particle is nearly the same. At this
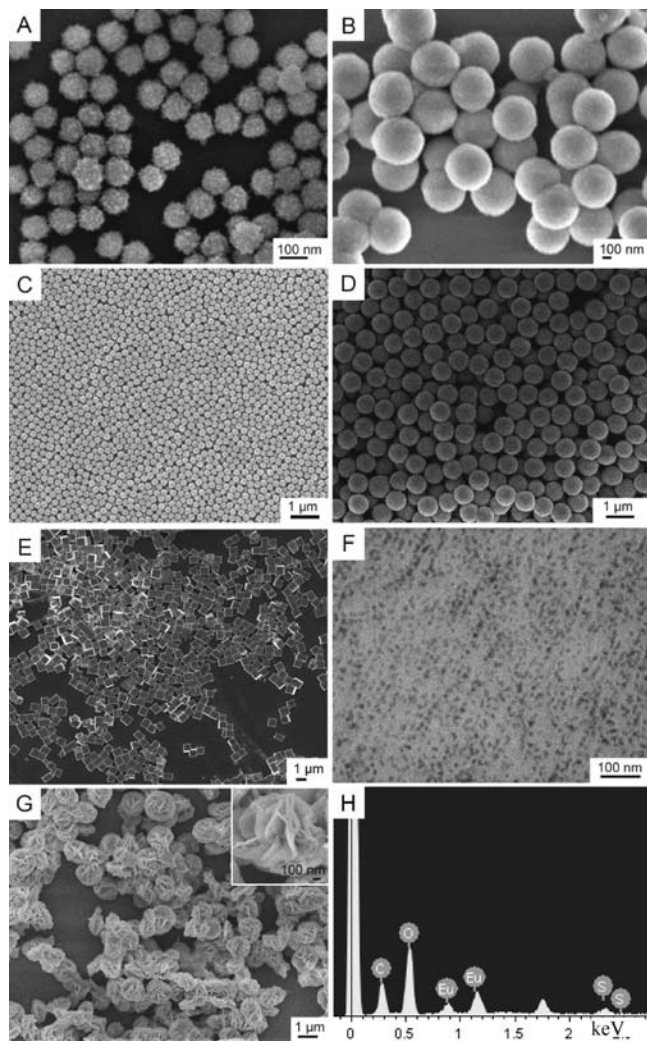
Figure 3. SEM images of ZnS (A, B), CdS (C), Cd$_{0.8}$Zn$_{0.2}$S (D), PbS (E), and Eu$_2$O$_2$S (G) colloidal particles, TEM image of Ag$_2$S (F), and EDS spectrum of Eu$_2$O$_2$S colloidal particles (H).

Figure 4. XRD patterns of various metal sulfide colloidal particles and corresponding JCPDS standard patterns (bars). The additional peaks marked with (+) can be indexed to Eu(NO$_3$)$_3$ (JCPDS 48-1073 and 27-1141).

late stage, no new "seeds" form, and the growths of all the particles are in a concurrent manner, leading to the formation of uniform final product.

This self-correcting reaction route is suitable for the preparation of highly uniform metal sulfide colloids when other metal cations are introduced into the synthetic system, as demonstrated in the following section.

General Synthesis and Properties of Metal Sulfide Colloidal Particles. Figure 3 displays the representative images of a series of metal sulfide colloidal particles. Highly uniform colloidal spheres of ZnS and CdS (Figure 3A−C), the two extensively studied II−VI semiconductors, have been obtained. The sizes of both ZnS and CdS particles are tunable from nanometer to submicrometer scale by simply varying the reaction parameters such as concentration, reaction temperature, and reaction time. Simply by varying the molar ratios of Zn(NO$_3$)$_2$ and Cd(NO$_3$)$_2$, highly uniform Cd$_{0.8}$Zn$_{0.2}$S colloidal spheres have also been afforded. The size distribution of the colloidal spheres can be controlled in a very narrow range with a standard size deviation smaller than 5%.

By changing the metal salts with other synthetic conditions being kept nearly identical, uniform PbS colloidal particles
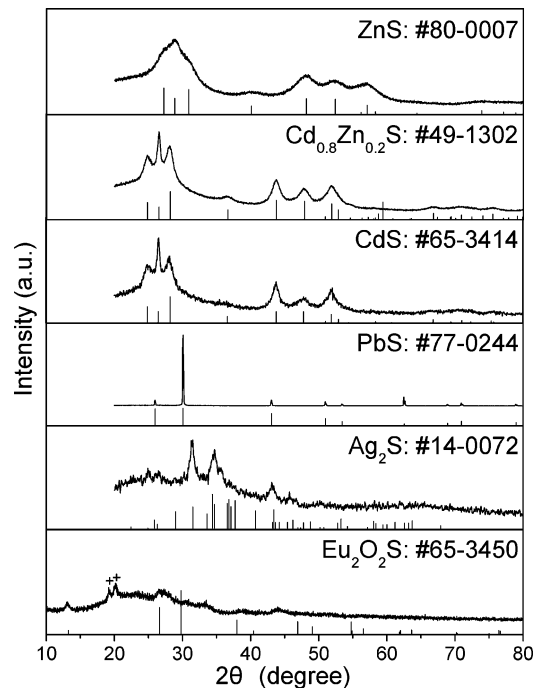
(IVA group, Figure 3D), and Ag$_2$S nanocrystals (IB group, Figure 3E) have also been obtained via this autocatalytic surface growth technique. The as-obtained products are all of pure phase according to the corresponding powder XRD patterns shown in Figure 4.

The colloidal particles of Eu$_2$O$_2$S, which proved to be difficult to obtain through a solution route,[28,29] were prepared in our system by using Eu(NO$_3$)$_3$ as the metal source. The composition of the material was confirmed by EDS (Figure 3H and Supporting Information, Figure S2). The resulting product with an average size of about 1 μm exhibits nearly monodisperse flower-like structures (Figure 3G). Further HRTEM images reveal that the main components of Eu$_2$O$_2$S colloidal particles are amorphous (left HRTEM image in Figure 5), while only a small proportion of each particle are crystalline (right HRTEM image in Figure 5). By measuring the lattice distances, some fringes are assigned to (100) and (011) facets of Eu$_2$O$_2$S (JCPDS 65-3450). Pink emission is observed for the particles suspended in ethanol (Supporting Information, Figure S3 left) upon illumination with a UV lamp. The strong and broad emission peaks at 615 and 743 nm are due to the forced electric dipole transition $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_5$ respectively (Figure 6 and Supporting Information, Figure S3 right). Other Ln$_2$O$_2$S colloids (see, for example, Supporting Information, Figure S4) with interesting optical properties may also be obtained through a similar synthetic strategy.

The metal sulfide colloidal particles we obtained belong to three different crystal structures (Figure 4): cubic for PbS,

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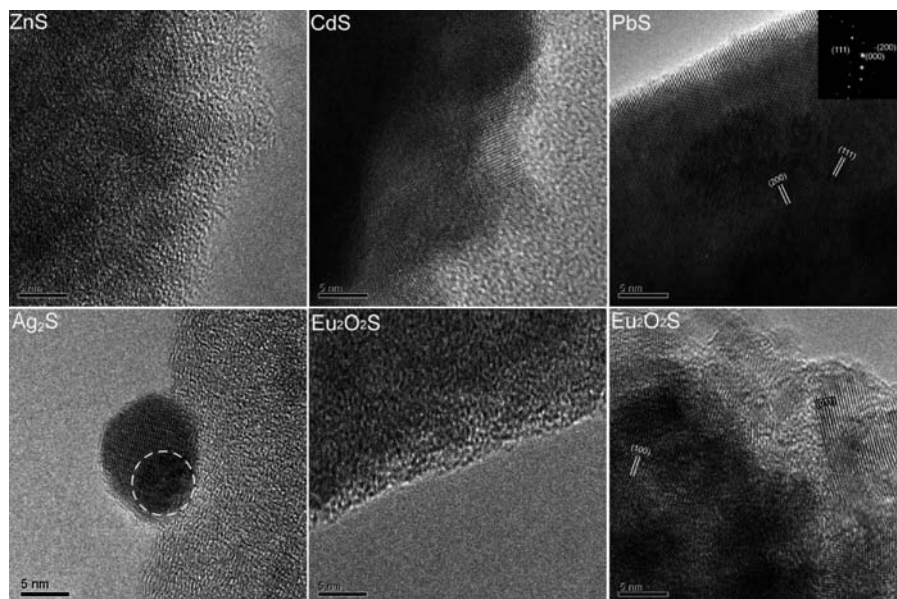(29) Zhao, F.; Yuan, M.; Zhang, W.; Gao, S. *J. Am. Chem. Soc.* **2006**, *128*, 11758–11759.

Figure 5. HRTEM images of various metal sulfide colloidal particles. Inset: selected area electron diffraction pattern. The HRTEM image of Ag_2S in the white circle shows the fringes of Ag formed from reduction of Ag_2S because of irradiation of electron beam.
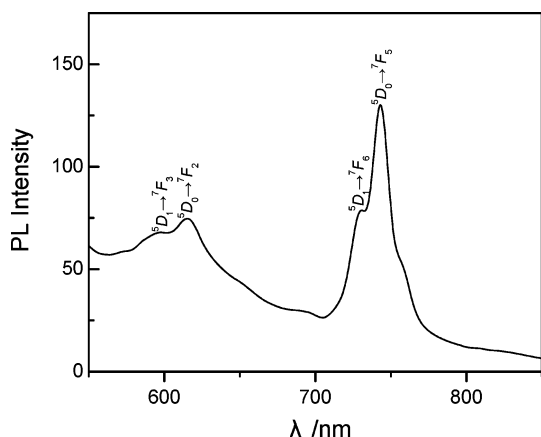

Figure 6. Photoluminescent spectrum of Eu_2O_2S colloidal particles.

hexagonal for ZnS, CdS, $Cd_{0.8}Zn_{0.2}S$, and Eu_2O_2S, and monoclinic for Ag_2S. The HRTEM imaging (Figure 5) reveals that the submicro/micrometer sized colloidal particles (except for PbS) are composed of smaller nanocrystals, and this explains why the XRD peaks of the colloidal particle samples other than the PbS are distinctly broadened (Figure 4). The PbS colloidal particles (1 μm in size) with fringes assignable to (111) and (200) facets of PbS (JCPDS 77-0244) are all single crystalline, and the XRD peaks of these particles are hence rather sharp.

Because of high uniformity and regular shape of ZnS, CdS, and $Cd_{0.8}Zn_{0.2}S$ colloidal spheres, these particles can easily assemble into close-packing films as shown in Figure 7. The narrow size distribution of the colloidal particles leads to ordering of particles into secondary structures. From the amplified SEM images, it is seen that two-dimensional cubic close-packing of CdS and hexagonal close-packing of both ZnS and CdS form easily at a relatively high cover level simply by drop-casting their colloidal solution in ethanol on silicon substrates. Ag_2S nanocrystals can also be utilized to prepare a homogeneous film via drop casting as shown in Figure 7. More importantly, all the colloidal particles

obtained in our current system are hydrophilic and are able to be dispersed well in water and other polar solvents. The colloidal solution of these particles remains stable for several hours to several months, depending on their size and shape. Because of ease in preparing a large-area film via low-cost techniques (such as drop casting, spin coating, ink-jet printing), it is envisioned that these metal sulfide colloidal particles are useful for fabrication of various functional devices such as chemical sensors, optoelectronic devices, solar cell, and so on.

Formation Mechanism. On the basis of the experimental results, the formation mechanism in our synthetic system can be summarized in Scheme 1. According to previous work,[23−25] TU is decomposed mildly and continuously in the reaction system in the presence of metal cations (M^{x+}) at a temperature much lower than the temperature at which pure TU decomposes even under the protection of N_2.[24] Upon the release of $S^{2−}$ because of decomposition of TU, metal sulfide nanocrystal clusters form in situ and then these clusters aggregate into small cores as "seeds" for the following growth of $MS_{x/2}$ colloidal particles. In this process, the as-obtained $MS_{x/2}$ cores act as a catalytic surface[23−25] to prompt further TU decomposition and the in situ formation of extra $MS_{x/2}$ clusters on the core surface, resulting in mild but continuous growth of colloidal particles. Because the final colloidal particles are actually formed through aggregation of nanocrystals, the shapes of the colloidal particles do not depend on the crystal structures of the corresponding compounds, and the appearance of spherical or semispherical (flower-like) morphologies for the colloidal particles is not surprising.

Alternatively, the initially formed nanocrystal clusters undergo no aggregation but grow directly to form uniform single crystal colloidal particles with a micro/submicrometer size. The $MS_{x/2}$ nanocrystals and the subsequently formed larger crystals, which are equivalent to the above-mentioned
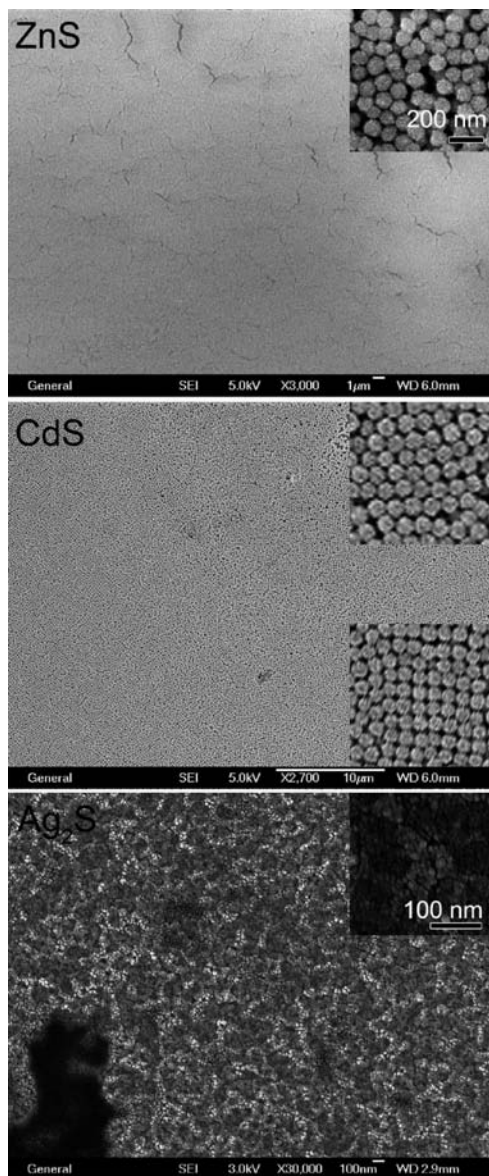
Figure 7. SEM images of large-area films formed by drop-casting 100 nm ZnS and 280 nm CdS colloidal spheres, and ~10 nm Ag$_2$S nanocrystals on silicon substrates. Inset: corresponding amplified image.

MS$_{x/2}$ cores, act as a catalytic surface as well for the TU decomposition. In this case (e.g., PbS cubes), the shape of the formed colloidal particles is closely correlated with the crystal structure of the corresponding compound.

For Ag$_2$S, no obvious further growth of the as-formed nanocrytal clusters was observed. After the Ag$_2$S nanocrystals were formed, prolonged reaction time did not lead to particle size increase but to broadened size distribution, probably because of Ostwald ripening (Supporting Information, Figure S5). A reasonable explanation for this observation is that most of the AgNO$_3$ and TU are consumed up immediately after the formation of Ag$_2$S nanocrystals because of the high reactivity of AgNO$_3$. The whole growth process of Ag$_2$S colloid particles stops at the first stage shown in Scheme 1 because of the lack of reactants (TU and AgNO$_3$) at the following stages, and therefore uniform Ag$_2$S nanocrystals are finally obtained in the present synthetic system.

Scheme 1. Formation Mechanism of Metal Sulfide Colloidal Particles, $x = 2$ or 3
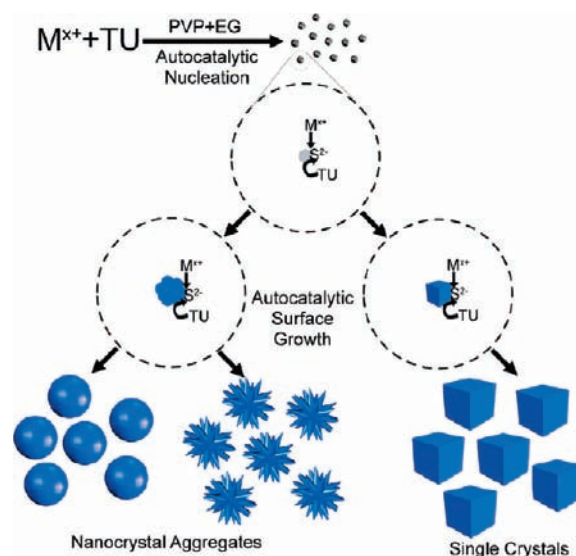
Effect of Metal Salt Anions. The anions of the metal salts used as reactants show significant effect on the morphology and size of the colloidal spheres. For example, the size of ZnS colloidal spheres increases from about 100 nm (Figure 3A) to 540 nm (Figure 3B) by replacing Zn(NO$_3$)$_2$ with ZnSO$_4$ as Zn source (Table 1). Meanwhile the morphology of CdS colloidal spheres can also be varied by choosing different cadmium salts (Cd(NO$_3$)$_2$, Cd(CH$_3$COO)$_2$, and CdCl$_2$), as shown in Supporting Information, Figure S6. The anions play a key role in controlling the assembly manner of the primary CdS nanocrystals, which are of similar size for different cadmium salts, into CdS secondary particles. It is believed that these anions selectively bind to specific facets of the primary nanocrystals, leading to surface energy difference among various facets.[29−31] The facets with higher energies tend to grow or to assemble with other nanocrystals. In this way, the growth rate and the assembly manner of the primary nanocrystals is somehow governed by the anions. The effect of anions in the reaction sources is obviously very important because the structural feature and thus the property of the resulting colloid particles depend on the anions to a considerable extent. Our reaction system involves only four components (EG, metal salt, TU, and PVP), and it is possible to systematically investigate the effects of various anions and other chemical additives by monitoring the morphological evolution of the colloidal spheres.[30,31] Further detail on the effect of anions will be reported elsewhere.

Effect of PVP. PVP plays multiple roles in our synthetic system. First, as a stabilizer, PVP protects the product from agglomeration both in the mother solution and in the as-obtained powder.[32] The content of PVP could reach a percentage value higher than 20% in the flower-like colloidal particles as confirmed by EDS (for example, Eu$_2$O$_2$S, Figure 3H and Supporting Information, Figure S2) because of the

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high surface area of the particles. Second, PVP molecules with a molecular weight (MW) of 58,000 may be used to regulate the viscosity and diffusion coefficient of the reaction system. For instance, by increasing the concentration of PVP in the synthetic system of CdS colloids, the diffusion coefficient is reduced to a great extent, resulting in the decrease of the particle size without an obvious change in particle shape.[24] Finally, as a capping agent or ligand, PVP in combination with the NO_3^- anions directs the formation of various metal sulfide colloidal particles with unique shapes. When other anions (for example, CH_3COO^- and Cl^-, Supporting Information, Figure S6), which interact with the colloidal particle surface more strongly, are introduced into the reaction system, the effect of PVP and NO_3^- is suppressed,[30−33] and the morphology of the product is altered accordingly.

Key Synthetic Parameters for Uniform Colloids. On the basis of our observations, it is possible to draw a general conclusion about how to prepare uniform colloidal particles in the current system. The key factors are the preparation of the homogeneous stock solution, the proper concentration of PVP which stabilizes the as-formed particles,[24] the relatively slow and continuous formation of $MS_{x/2}$ clusters which depends on the reaction temperature, and the concentration of metal salt source.

Reaction temperature influences the morphology of the colloidal particles to a great extent. The reaction temperature should not be higher than the decomposition temperature of TU (~180 °C) because otherwise the TU would be pyrolyzed rapidly and products with irregular shapes would be formed. Taking PbS for example, we could get uniform cubes with a size of ~1 μm at a relatively low reaction temperature (<120 °C). When the mixed solution of TU, $Pb(NO_3)_2$, and PVP in ethylene glycol was treated at a temperature of 140 °C or higher, we could only get PbS dendrites sized in several micrometers as shown in Figure 8. Lower temperature is conducive to the formation of uniform particles and is also environmentally benign on the other hand.

The concentration of metal salt affects the formation rate of $MS_{x/2}$ materials. Taking PbS as the example again, a high concentration (>0.5 M) of metal salt triggers the formation of the corresponding metal sulfide even at room temperature, while the stock solutions with a low concentration (<0.05 M) of metal salt is stable for several days.

To achieve the self-correcting growth, mild reaction parameters, including relatively low temperature and suitable concentration of metal salt, are highly desirable to ensure the slow and continuous nanocluster formation and fast autocatalytic surface growth without the formation of new "seeds".

Conclusions

An autocatalytic surface growth mechanism for metal sulfide colloidal particles has been unambiguously demon-
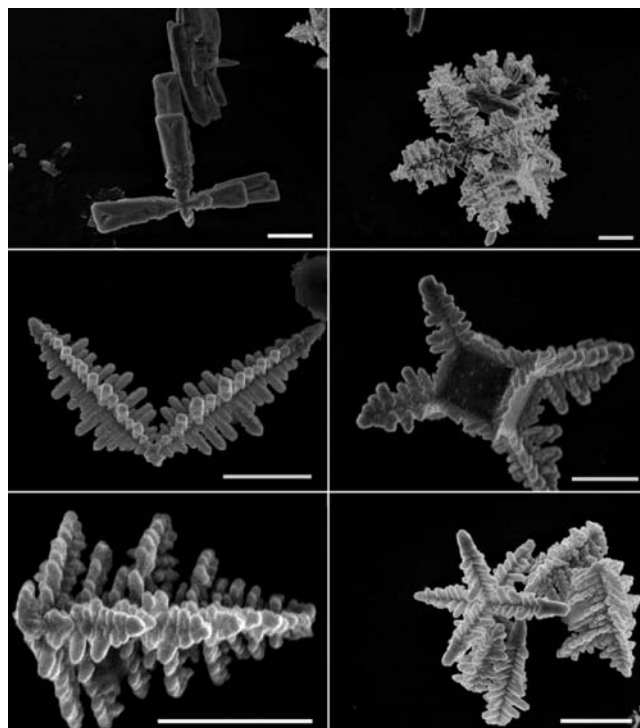
(33) Xiong, Y.; Wahio, I.; Chen, J.; Cai, H.; Li, Z.-Y.; Xia, Y. *Langmuir* **2006**, *22*, 8563–8570.

Figure 8. PbS dendrites formed at a higher temperature (140 °C). Scale bar: 1 μm.

strated. Unlike in the conventional synthetic systems, the growth process in our system exhibits self-correcting behavior, that is, the broad size distribution at the early stage becomes narrower at the later stage of the growth process. Under optimal experimental conditions, the sizes of the monodisperse colloid particles remain highly uniform for a long time during the reaction. This simple synthetic approach has been adopted to prepare not only uniform mesoscale colloidal particles but also more complex anisotropic structures of various metal sulfides.

In principle, by choosing proper self-catalytic reactions involving other reagents (such as selenourea, urea, etc.) and metal cations, important colloidal particles of different metal chalcogenides may be prepared in a similar way. Our results open vistas for the green preparation of uniform colloidal particles. The resulting uniform functional colloidal particles, well dispersible in water and various common organic polar solvents, should be ideal building blocks for fabricating advanced functional devices via low-cost solution phase techniques.