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Controllable Growth of Ag_2S-CdS Heteronanostructures

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ABSTRACT: High quality Ag_2S-CdS heteronanostructures were prepared *via* a facile one-pot method, which is based on the co-thermal decomposition of two single-source precursors of $(C_2H_5)_2NCS_2Ag$ and $((C_2H_5)_2NCS_2)_2Cd$ in a mixture of oleylamine and oleic acid. Ag_2S-CdS heteronanostructures with spherical and matchstick-like structures can be easily obtained in high yield by careful control of the growth kinetics. It was found that oleic acid is conducive to the formation of spherical Ag_2S-CdS heteronanostructures and oleylamine helps to the formation of matchstick-like Ag_2S-CdS heteronanostructures. Variable-temperature powder X-ray diffraction studies confirmed the heteroepitaxial growth of CdS on tiny Ag_2S nanocrystals, in which Ag_2S nanocrystal plays a catalytic role in the epitaxial growth of CdS segments.

1. Introduction

Development of sophisticated colloidal chemical routes had enabled the preparation of compositionally and morphologically intricate nanostructures in the past few decades. Diversity of properties had particularly been achieved through combination of distinct material domains in a heterostructured nanocrystal, each characterized with their specific physical properties, surface chemistry, and morphology. Modifying properties of the individual moieties as a result of the coupling between the two different domains were often observed to emerge through interactions at the shared interface, which might lead to energy, spin and charge transfer.[1] Multifunctional HNSs will be quite useful in a broad range of applications such as catalysis, biomedical, photovoltaic devices, sensors, and so on, which can not be met by single nanoparticles or the mixture of different nanoparticles.[2]

In last decade, heteronanostructuresmainly contains metal-metal,[3] metal-semiconductor,[4] metal-oxide[5] and oxide-semiconductor.[6] Semiconductor-semiconductor HNSs were extensive prepared by wet chemical method in recent years, including Cu_2S-ZnS,[7] Cu_2S-In_2S_3,[8] Cu_2S-$CuInS_2$,[9] Cu_2S-$CuInZnS_x$,[10] Ag_2S-ZnS,[7,11] Ag_2S-CdS,[12] Ag_2S-$CuInS_2$,[13] Ag_2S-$AgInS_2$,[14] Ag_2S-ZnSe,[7a] Ag_2Se-ZnS,[15] and Ag_2Se-ZnSe.[16] In the process of synthesis of these

semiconductor-semiconductor heteronanostructures (HNSs), Cu_2S, Ag_2S and Ag_2Se usually as seeds were firstly synthesized, and then grew the nanocrystals of the second materials on the end of the seeds. Recently, we constructed the well-defined matchstick-shaped Ag_2S-ZnS HNSs *via* a one-pot thermal decomposition of two single-source precursors method, and it was found with excellent near-infrared (NIR) and UV/blue emissions.[11a] When we doped Mn, the HNSs exhibited multicolor emissions of blue, orange, and NIR.[11b] Inspired by these, we carried out the study of Ag_2S-CdS HNSs. Most of the reports used of cation exchange method to obtain the Ag_2S-CdS HNSs,[17] and there were also some reports by a wet chemical method[12]. Xu *et al*. synthesized Ag_2S-CdS HNSs, using Ag_2S nanocrystals acted as catalyst for growth of CdS nanorods.[12a] Huang *et al*. used one-pot hydrothermal method for the fabrication of Ag_2S-CdS HNSs with high uniformity in morphology.[12b] But facile synthesis approach is still a challenge for controlled growth of Ag_2S-CdS HNSs.

Herein, we reported the successful synthesis of high quality spherical and matchstick-like Ag_2S-CdS HNSs by using our previously reported single-source precursor method.[11,18] That is, thermal decomposition of two single-source precursors of $(C_2H_5)_2NCS_2Ag$ (Ag(Ddtc), Ddtc =diethyldithiocarbamate) and $Cd(Ddtc)_2$ in a mixture of oleylamine (OM) and oleic acid (OA), in which uniform Ag_2S-CdS HNSs were obtained in high yield. The length of the CdS could be easily tuned by increasing the amount of $Cd(Ddtc)_2$. The size, shape and crystalline phases of as-obtained Ag_2S-CdS HNSs were systematically characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). We found that the growth mechanism of HNSs was that Ag_2S crystals nucleate firstly, and then it served as seeds and catalyst to guide the growth of CdS segments. OA is conducive to the formation of spherical Ag_2S-CdS HNSs and OM helps to the formation of matchstick-like Ag_2S-CdS HNSs.

2.Experimental Section

2.1. Chemicals

Oleylamine (OM; 80-90%, Aladdin), oleic acid (OA; 90%, Aldrich), $AgNO_3$, $CdCl_2$, $(C_2H_5)_2NCS_2Na{\cdot}3H_2O$ (Na(Ddtc)), ethanol (AR), cyclohexane (AR) (Sinopharm Chemical Reagent Company). All chemicals were used as received without further purification.

2.2. Preparation of Ag(Ddtc) and $Cd(Ddtc)_2$

The preparation of single-source precursors of Ag(Ddtc) and $Cd(Ddtc)_2$ was referred to our previous reports.[18] In a typical reaction for Ag(Ddtc), 0.05 mol of $AgNO_3$ and Na(Ddtc) were firstly dissolved in 100 mL of distilled water, respectively. Then, the two solutions were mixed with stirring in a 250 mL beaker. After constant stirring at ambient condition for 2 h, the resulting yellow precipitate was filtered, washed with distilled water, and dried in air at 60 ^{o}C. $Cd(Ddtc)_2$ was also prepared by the same way depicted as above, except the molar ratio of cadmium chloride dehydrate to Na(Ddtc) was 1 to 2.

2.3. Synthesis of Ag_2S nanocrystals and CdS nanocsrystals

The preparation of Ag_2S nanocrystals was carried out in an air-free condition. In a typical procedure, a mixture of Ag(Ddtc) (0.026 g, 0.1 mmol), OM (5.36 g) and OA (5.65 g) were loaded in a 100 mL three-necked flask. The mixture was degassed under a vacuum for 5 min at room temperature. The reaction system was then filled with argon, and its temperature was increased to 170 ^{o}C and kept for 60 min. Then it was allowed to cool down to room temperature naturally. And 50 mL of ethanol was poured into the solution, the resultant mixture was centrifugally separated and the products were collected.

The synthetic procedure for CdS nanocrystals is similar to that of Ag_2S nanocrystals, but the mixture is composed of $Cd(Ddtc)_2$(0.04g, 0.1 mmol), OM (10.72 g) and OA (0.02 g).

2.4. Synthesis of Ag_2S-CdS HNSs

The synthetic procedure was the same as that for synthesis of Ag_2S nanocrystals. For the synthesis of spherical Ag_2S-CdS HNSs, the mixture used here is Ag(Ddtc) (0.026 g, 0.1 mmol), $Cd(Ddtc)_2$ (0.008g, 0.02 mmol), OM (5.36 g) and OA (5.65 g). For the synthesis of matchstick-like Ag_2S-CdS HNSs, a mixture of Ag(Ddtc) (0.026 g, 0.1 mmol), $Cd(Ddtc)_2$ (0.02g, 0.05 mmol), OM (10.72 g) and OA (0.02 g) were used. The Ag_2S-CdS HNSs with varied length could be obtained by changing the amount of $Cd(Ddtc)_2$ (0.02g-0.08g).

2.5. Characterization

The size, morphology and high-resolution transmission electron microscopy (HR-TEM) characterization were examined by a Tecnai G2 F20 S-Twin TEM (FEI, USA) operated at 200 kV and equipped with an energy dispersive X-ray spectroscopy (EDS). TEM samples were prepared by a drop-casting technique by putting 1 drop of the cyclohexane solution onto a carbon-coated Cu grid, and the solvent was evaporated at room temperature in the air. Powder X-ray diffraction

(XRD) patterns of the dried powders were recorded on a Bruker D8 Advance powder. X-ray diffractometer at a scanning rate of 4^{o} min^{-1}, using Cu-Kα radiation (λ=1.5406 Å) in the range of 20-60^{o}.

3. Results and Discussion

Morphology of heteronanostructures

Figure 1 indicates typical TEM images of morphologies of Ag_2S nanoparticles and Ag_2S-CdS HNSs with different lengths of CdS segment at low magnification. As shown in Figure 1a, the as-prepared Ag_2S nanocrystals are uniform with a size of ~20 nm. The difference in the contrast suggests that the two segments are composed of different materials showed in Figure 1b-d. The dark spheres are Ag_2S, and the parts of brighter are CdS. The length of CdS segments is elongated with increasing the amount of $Cd(Ddtc)_2$: (b) Ag_2S : CdS =1:0.4, (c) Ag_2S : CdS =1:1, (d) Ag_2S : CdS =1:2(mole ratio). The nanocrystals are directly used in the consequent preparation without further separation and purification. The size of the HNSs is also about 20 nm in Figure 1b, which is similar to the size of single Ag_2S nanocrystals in Figure 1a. When the Ag_2S/CdS molar ratio is changed to 1:1, the Ag_2S heads have a mean diameter of 17 nm and the CdS stems is 14×22 nm shown in Figure 1c. However, at the Ag_2S/CdS molar ratio is 1:2, the average diameter of the Ag_2S is only about 13 nm and the CdS segment is 12×33 nm (Figure 1d). These data are extracted from 100 obtained nanocrystals. We observe that the size of Ag_2S is reduced with the increase of the length of CdS segments.

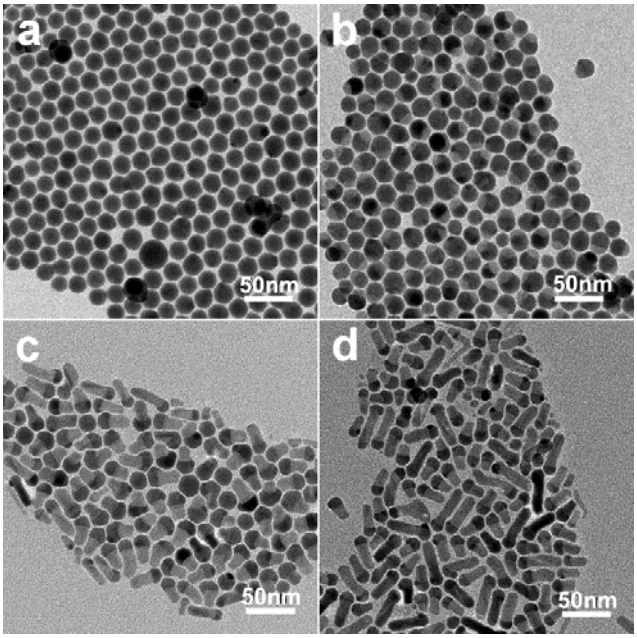

Figure 1. TEM images of Ag_2S (a), Ag_2S-CdS HNSs prepared at different Ag_2S/CdS molar ratios: (b) 1:0.4, (c) 1:1, and (d) 1:2.

HRTEM images are able to resolve the atomic structure of the Ag_2S and CdS phases in HNSs. Based on the analysis of the corresponding crystal lattices, the spherical head is composed of Ag_2S and the stem is CdS, and the Ag_2S-CdS conjunction interface and the corresponding FFT images are shown in Figure S1. It can be observed the interface orientation relationships between Ag_2S and CdS are $(-111)_{Ag2S}$ // $(002)_{CdS}$. The lattice mismatches along this direction are 1.2% (Figure 2c). The (101) plane of CdS is further confirmed by a higher quality HRTEM image (Figure 2d), and the CdS double layers along the [101] direction could be clearly observed. This is a strong evidence that d = 0.32 nm corresponds to the (101) plane of hexagonal CdS. Detailed information on the structure and local atomic composition of the Ag_2S-CdS HNSs are further acquired with EDX line scanning under the STEM mode. The elemental profiles in Figure 3 show that Ag is limited to the head and Cd to the stem part, while S is dispersed throughout the HNSs. Based on the results of the EDX analysis, it further evidences that the head of nanocrystals is Ag_2S and the stem is CdS.

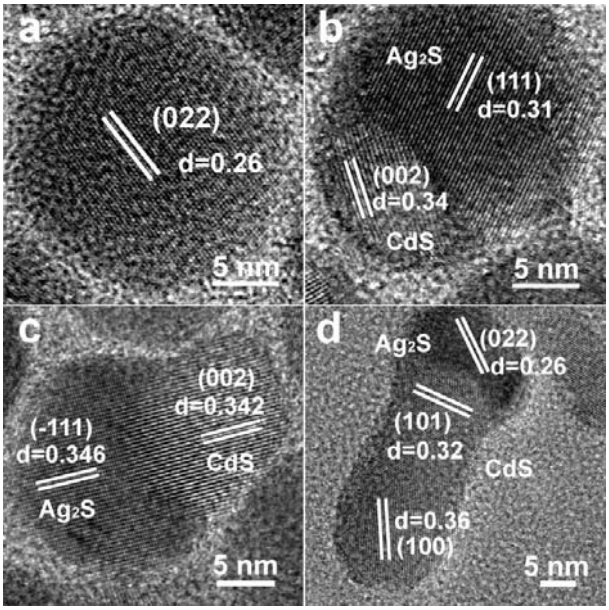

Figure 2. HRTEM images of Ag_2S (a), Ag_2S-CdS HNSs prepared at different Ag_2S/ CdS molar ratios: (b) 1:0.4, (c) 1:1, and (d) 1:2.

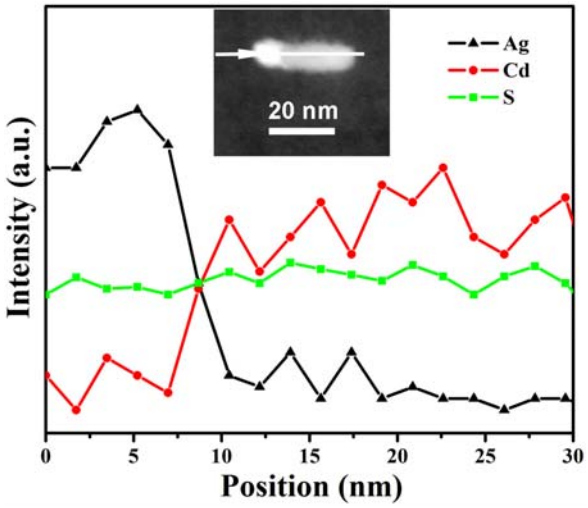

Figure 3. Elemental profiles of Ag, Cd, and S in the obtained Ag_2S-CdS HNSs. The EDX line scan was recorded along the white line shown in panel.

Growth mechanism

In the previous reports of Ag_2S-CdS HNSs, Ag_2S nanocrystals usually served as nanoseeds to catalyze the growth of CdS segments were prepared firstly. In this experiment, however, precursors of Ag(Ddtc) and $Cd(Ddtc)_2$ were added in OM and OA at the same time. So it is important to investigate the growth mechanism of our Ag_2S-CdS HNSs. During the synthesis, we observed that the color of the reaction mixture changed with the elevating of temperature from 90 ^oC to 170 ^oC. In order to understand the growth mechanism deeply, we monitored the growth process of Ag_2S- CdS HNSs with molar ratio of 1:1 using XRD. The results (Figure 4) show that

Ag_2S nanocrystals were formed preferentially at 90 ^oC and CdS were formed later at 120 ^oC, as their characteristic diffraction peaks were clearly indexed. The XRD patterns indicate that Ag_2S crystallized in its typical monoclinic structure, P21/n phase (a=4.229 Å, b=6.931 Å, and c=7.862 Å). The CdS of the HNSs are consistent with a hexagonal phase, P63mc (a=b=4.141 Å, c=6.720 Å). These results indicate that Ag_2S nanocrystals were formed firstly at 90 ^oC, and then Ag_2S nanocrystals were served as seeds to guide the growth of CdS stems.

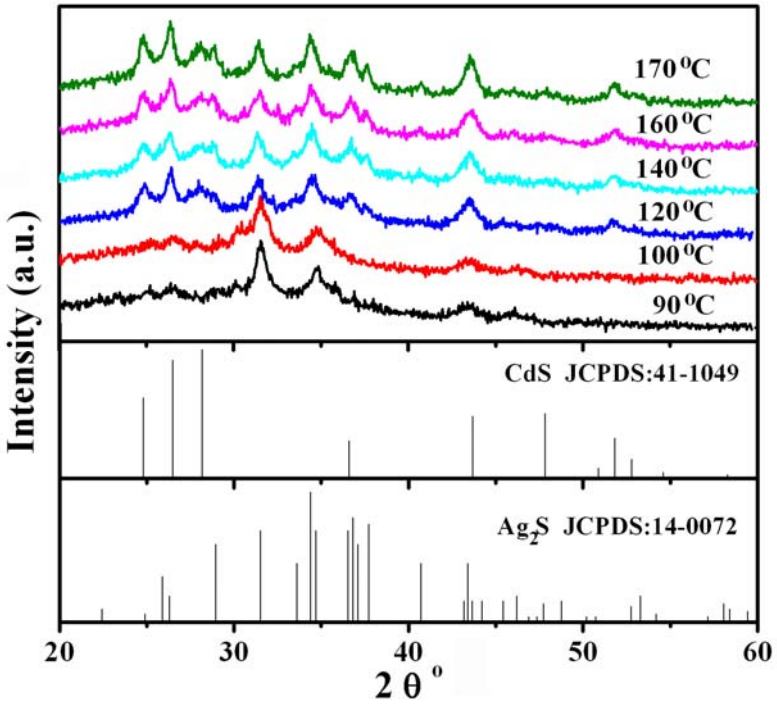

Figure 4. XRD patterns of the evolution of Ag_2S-CdS HNSs.

Whether Ag_2S catalyze the growth of CdS? To figure out this problem, we prepared CdS nanocrystal in absence of Ag(Ddtc) at 120 ^oC, 170 ^oC and 250 ^oC, respectively. And we examined the samples by XRD. As shown in Figure 5, the sample prepared at 120 ^oC for 1 h did not have obvious diffraction peaks, and the board diffraction peaks appear at 170 ^oC. All of the characteristic diffraction peaks become very evident until 250 ^oC. The results demonstrate that Ag_2S nanocrystal plays a catalytic role in the epitaxial growth of CdS stems. Therefore, the growth mechanism of HNSs can be concluded to be seeded and catalyst-assisted growth *via* a one-pot method. Also because of this, the production rate of Ag_2S-CdS HNSs is very high by thermal decomposition of two single-source precursors, and the parts of CdS can continue to grow longer by increasing the proportion of $Cd(Ddtc)_2$ (Figure 6a).

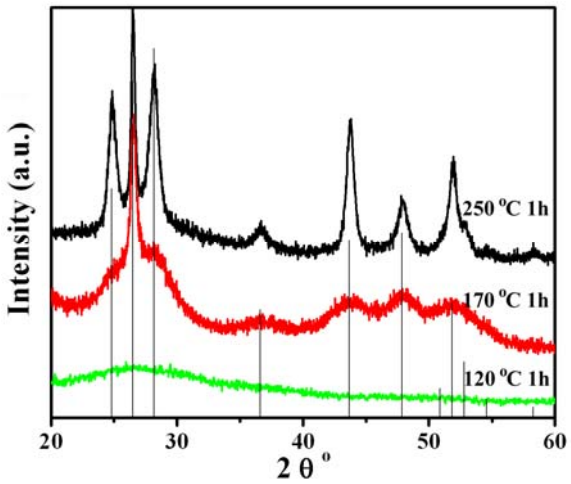

Figure 5. XRD patterns of CdS nanocrystals prepared at different temperature (120 °C, 170 °C and 250 °C).

Reaction conditions effect

OM and OA had been used as surface modification agents and solvents in this study, which played a vital role in controlling the morphology of Ag_2S-CdS HNSs. Ag_2S-CdS spherical HNSs was prepared with the molar ratio of OM/OA at 1:1 as showed in Figure 1b (Ag_2S : CdS =1:0.4). When the Ag_2S/CdS was 1:1, the shape is also spheres (Figure 6b). But the particles are non-uniform, and generate a large number of isolated CdS nanoparticles. In contrast, the uniform Ag_2S-CdS (Ag_2S : CdS =1:1) matchstick-like HNSs were synthesized under the condition of excess OM. The length of the HNSs could be controlled easily by changing the amount of CdS. It can be attributed that OA tends to make the nancrystals isotropy[19] and OM facilitates the growth of one-dimensional nancrystals by specifically binding to a certain crystal facet[20]. It determines the growth of CdS stem of Ag_2S-CdS matchstick-like HNSs along the [101] direction in our case (Figure 2d). As illustrated above, using this facile method, well defined Ag_2S-CdS HNSs with different shapes can be synthesized by tuning the composition of solvents and precursors. In addition, the influence of reaction temperature (150-190 °C) and reaction time (30-120 min) on the morphology of Ag_2S-CdS HNSs (Ag_2S/CdS molar ratios: 1/1)was also investigated (Figure S2). Interestingly, either changing the synthetic temperature to 150 °C and 190 °C or varying the reaction time to 30 min or 120 min, irregular Ag_2S-CdS HNSs were obtained. These results suggest that the reaction at 170 °C for 60 min is an optimized condition for preparation of uniform Ag_2S-CdS HNSs in this system.

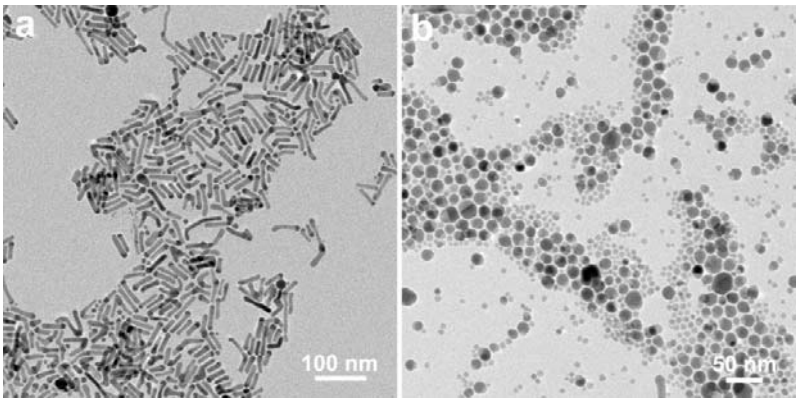

Figure 6. TEM image of Ag_2S-CdS HNSs at different conditions. (a) OM/OA(10.72g/0.02g), (b) OM/OA(5.36g/5.65g).

In summary, high quality spherical and matchstick-like Ag_2S-CdS HNSs were prepared via a facile one-pot method, by which two single-source precursors of Ag(Ddtc) and $Cd(Ddtc)_2$ were co-thermal decomposed in a mixture of OM and OA. The length of the HNSs could be easily controlled by increasing the amount of $Cd(Ddtc)_2$. It was found that the growth mechanism of HNSs is that Ag_2S nanocrystals nucleate firstly, and then they served as seeds and catalyst to guide the growth of CdS segments. Additionally, OA tends to guide the formation of spherical HNSs, and OM prefers to form matchstick-like Ag_2S-CdS HNSs.

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Notes and references

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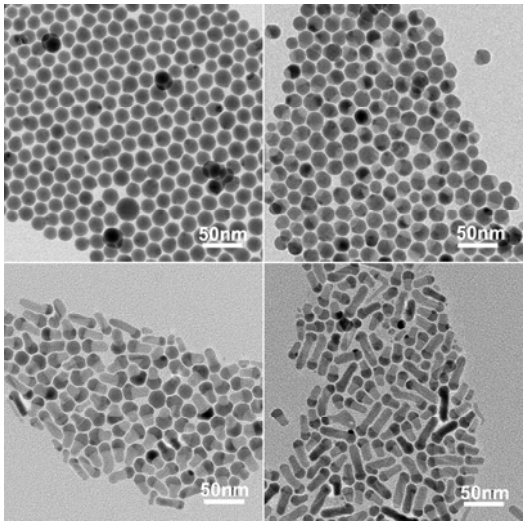

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