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A facile chemical route to semiconductor metal sulfide nanocrystal superlattices†

Zhaoping Liu, Jianbo Liang, Dan Xu, Jun Lu and Yitai Qian*
Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China. E-mail: ytqian@ustc.edu.cn

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We report a facile chemical route for the synthesis of monodisperse nanocrystals of various metal sulfides (PbS, Cu_2S, and Ag_2S) and their assemblies into nanocrystal superlattices (NCSs); the sulfides NCSs were precipitated by adding ethanol to nanocrystal colloids, which were obtained directly by a reaction between metal thiolate and thioacetamide in a pure dodecanethiol solvent.

In the past several years, the assembly of monosized nanocrystals into nanocrystal superlattices (NCSs) has attracted much attention because these mesostructures present new physical properties differing from those of isolated nanocrystals and those of the bulk phase.[1] The acquirement of such ordered superstructures would provide an opportunity to explore the collective physical properties of the arrays and develop further optical and memory devices.[2] The formation of NCSs in nanocrystal colloids can be generally achieved by the evaporation of solvents on a support[3] or the precipitation of nanoparticles through the addition of non-solvents.[4] In any case, it always relies on highly monodispersed nanocrystals. Currently a wide range of available monodisperse metal,[3b,c,4b,d] semiconductor,[3a,d,4a] magnetic metal alloys,[4c] and oxide[3e,f] nanocrystals can be used as building blocks for the fabrication of NCSs. Among these nanocrystals, semiconductor sulfide nanocrystals have been the most studied due to their quantum confinement effects and size-tunable optical properties.[5] Various synthetic schemes have been developed for the size- and shape-controlled synthesis of monodisperse metal sulfide nanocrystals, using organometallic precursors,[5a,b] coordinating solvent,[5d,6] non-coordinating solvent,[5c] reverse micelles,[3a,3d] microemulsions,[7] polymer films,[8] or solventless thermolysis techniques.[9] Whatever the method, it requires the presence of stabilizing ligands for controlling the size, shape and monodispersity of particles, and for favoring their self-assembly. The usually used ligands include long-chain phosphine,[5a,b] amine,[5d,6b] phosphine acid,[6a] carboxylic acid,[5c,e] and so on. In some cases, the synthesises were successfully performed by directly using these ligands as the coordinating solvents.[5d,6b] As we know, dodecanethiol ($C_{12}H_{25}SH$), another strong ligand for various metals, has been commonly used in the synthesis and assembly of noble metal nanoparticles.[3b,4b,10] The presence of a strong coordination effect of $C_{12}H_{25}SH$ suggests that it may be a potential ligand for the synthesis of metal sulfide nanoparticles. We here report that $C_{12}H_{25}SH$ can be used as an effective coordinating solvent for the synthesis of various sulfide nanocrystals. By using this solvent, we prepared monodisperse nanocrystals of PbS, Cu_2S and Ag_2S at a relatively low temperature (near 100 °C), and further precipitated them out as NCSs by adding ethanol to the formed nanocrystal colloids.

In our synthesis,† metal salts were dissolved in a warm solvent of $C_{12}H_{25}SH$ forming metal thiolates that were rapidly converted to metal sulfide nanocrystals upon the addition of thioacetamide (TAA). At the initial reaction stage, a bursting nucleation event occurred as evidenced by an immediate brown–black color change (for PbS synthesis). This process resulted in the generation of extremely small nanoclusters. Because the reaction was processed in a pure $C_{12}H_{25}SH$ solvent, these nascent nanoclusters would be fully capped by $C_{12}H_{25}SH$ molecules, leading to a very slow rate of nanocrystal growth. Moreover, the presence of copious capping molecules also strongly restricts particle coalescence. As a result, small-sized and monodisperse nanocrystals would be formed in this reaction system. The thiol-stabilized nanocrystals were well soluble in the thiol solvent. As described in previous reports,[4] adding a non-solvent (*e.g.* ethanol) to the resulting nanocrystal colloids might allow for the formation of NCSs.

Low-magnification transmission electron microscopy (TEM) observations show both PbS and Cu_2S samples consist of rod-like structures with diameters of over 100 nm and lengths of several micrometers (Fig. S1, ESI†). Fig. 1(a) presents a high-magnification TEM image of a single rod-like structure of PbS, clearly revealing the rod as highly ordered assemblies of monosized PbS nanocrystals with a mean diameter of 4.3 nm and an average interparticle distance equal to about 2.0 nm. Its selected-area electron diffraction (SAED) pattern (inset of Fig. 1(a)) exhibits small arcs of cubic rock-salt structure of PbS. Such discrete diffractions imply a high degree of orientational order being present in the collective atomic lattice, as illustrated in previous reports.[3c] Our high-resolution TEM study (Fig. S2, ESI†) reveals that the constituent PbS nanocrystals are well crystalline. Fig. 1(b) shows the TEM image of a rod-like structure of a Cu_2S nanocrystal superstructure. It can be observed that the component nanocrystals are slightly elongated with lengths of 4.5 nm and thicknesses of 3 nm. The SAED pattern, shown in the inset of Fig. 1(b), reveals a hexagonal (chalcoite) crystal structure of Cu_2S. This pattern also presents discrete diffractions, indicating orientational ordering of the hexagonal lattices of Cu_2S. It is well known that Cu_2S undergoes a phase transition at 105 °C from monoclinic to hexagonal structure.[11] Because of the higher synthetic temperature (120 °C), Cu_2S nanocrystals form with the hexagonal crystal structure. Compared with PbS and Cu_2S, the Ag_2S sample appears to be an amorphous assembly of nanoparticles (Fig. 1(c)). The inset of Fig. 1(c) shows a magnified view of a selected multilayer region, exhibiting a close-packed superlattice structure of monodisperse Ag_2S nanoparticles with size of about 3.2 nm.

X-Ray diffraction (XRD) was used to examine the as-prepared samples. Fig. 2(a)–(c) show the XRD patterns of PbS, Cu_2S and Ag_2S samples in which the broadening diffraction peaks can be

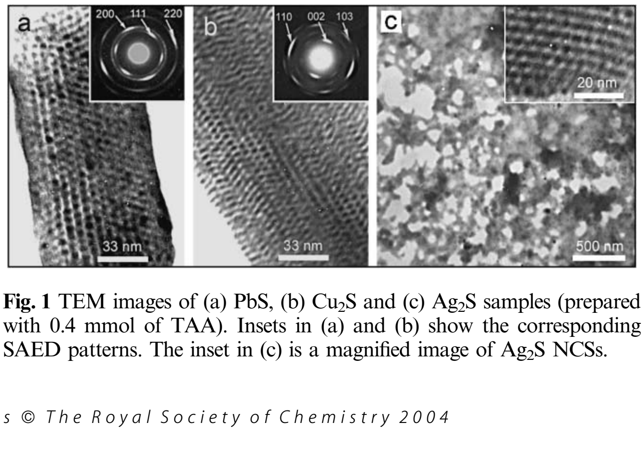

Fig. 1 TEM images of (a) PbS, (b) Cu_2S and (c) Ag_2S samples (prepared with 0.4 mmol of TAA). Insets in (a) and (b) show the corresponding SAED patterns. The inset in (c) is a magnified image of Ag_2S NCSs.

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† Electronic supplementary information (ESI) available: Experimental details, additional TEM images, XRD patterns, SEM images and TGA data. See http://www.rsc.org/suppdata/cc/b4/b409825k/

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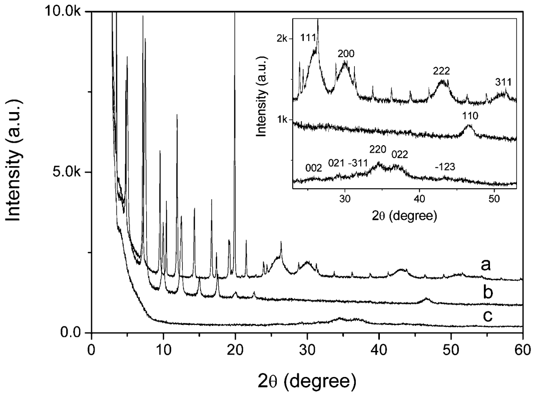

Fig. 2 XRD patterns of (a) PbS, (b) Cu_2S and (c) Ag_2S samples. Inset: enlarged patterns ($2\theta = 23–53°$).

indexed as the cubic rock-salt structure of PbS (JCPDS 5-595), hexagonal structure of Cu_2S (JCPDS 84-206), and monoclinic structure of Ag_2S (JCPDS 24-715), respectively. The corresponding patterns with 2θ in the range 23–53° are enlarged in the inset of Fig. 2. On the basis of the Scherrer equation, the broadening of the peaks is in accordance with their extremely small particle sizes, in accord with the above TEM observations. Moreover, a series of strong and sharp reflections at low angles in Fig. 2(a) and (b) can also be observed, which can be indexed to the layered structure of crystalline metal thiolate with an interlayer spacing of about 3.5 nm (Fig. S3, ESI†). Because the synthesis was performed with an insufficient amount of TAA, the presence of residual metal thiolate in the final colloids was expected. This means the obtained rod-like superstructures should be regarded as quasi-NCSs. For determining the content of remaining metal thiolate, the obtained samples were analyzed by thermogravimetric analysis (TGA). In the case of PbS samples, the TGA curve (Fig. S4, ESI†) indicates that the content of Pb thiolate was about 12.5%, very close to the calculated content of the remaining Pb thiolate in the nanocrystal colloids before the precipitation process.

Based on the above results, we presume that the formation of the rod-like superstructures may be related to the presence of the remaining metal thiolate. To understand the role of remaining metal thiolate (its content is dependent on the amount of used TAA) on the shapes of the products, we have systematically studied a series of PbS samples prepared by varying the amount of TAA. The XRD patterns (Fig. S5, ESI†) show that the diffraction peaks of metal thiolate were weakened and finally disappeared with increasing the amount of TAA from 0.44 to 0.5 mmol, and the corresponding TEM images (Fig. S6, ESI†) demonstrate that the proportion of rod-like structures decreases with this increase. The FESEM images (Fig. S7(a) and S7(b), ESI†) clearly show that the samples prepared with 0.44 mmol of TAA are composed of both rods ($\sim$85%) and grains ($\sim$15%), and the high-magnification TEM image (Fig. S7(c), ESI†) reveal that the both forms are nanocrystal superstructures. After a long time of electron beam irradiation, a layer of contamination with thickness of about 10 nm appears on the surfaces of the rods (Fig. S8, ESI†), most probably induced by the unstable Pb thiolate; such contamination was absent on the grains. These results indicate that only the rods contain crystalline Pb thiolate. We thus propose a possible mode for the rod-like quasi-NCSs. The rods may be a core–shell structure similar to a corn cob, in which nanocrystals are regarded as the corns and the crystalline metal thiolate is the core. Judging from both the low content of metal thiolate and the relatively larger diameters (about 100 nm) of the rods, we believe the shell should be multilayers of nanocrystals. In this mode, the remaining metal thiolate might preferentially precipitate out as rod-like structures, and then nanocrystals were spontaneously adsorbed on the rod surfaces in a assembled manner to form a corn cob-like and quasi-NCSs structure. However, we still need to obtain some direct evidences to support this mode. Further study on this topic is under way. When the amount of used TAA was increased to 0.5 mmol, the obtained samples are composed of faceted NCS particles with size of several hundred nanometers, as shown in Fig. 3(a). We also noted that the case of Cu_2S was similar to that of PbS. However, as described above, we did not obtain rod-like superstructures of Ag_2S by a similar procedure. The XRD pattern (Fig. 2(c)) reveals that the Ag_2S NCSs sample does not contain any crystalline Ag thiolate. This means that the remaining Ag thiolate can not develop into a crystalline phase under the present conditions and it simultaneously disturbs the assembly of nanoparticles into 3D NCSs. When using 0.5 mmol of TAA, well-defined granular particles with size of $\sim$100 nm were produced (Fig. 3(b)). A high-magnification image (inset in Fig. 3(b)) reveals these grains to be a 3D superlattice assembly of 3.2 nm-sized Ag_2S nanoparticles.

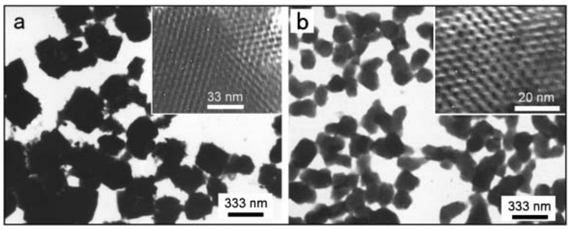

Fig. 3 TEM images of (a) PbS and (b) Ag_2S NCSs prepared with 0.5 mmol of TAA, respectively. Insets show the selected-area high-magnification image of a NCS particle.

In summary, monodisperse nanocrystals of various sulfides have been formed directly in $C_{12}H_{25}SH$, and have been self-assemblied into NCSs *via* a precipitation process. It was found that the remaining metal thiolate was responsible for the formation of rod-like quasi-NCSs of PbS and Cu_2S. Since the obtained nanocrystals are exceptionally monodispersed, and the present synthesis is simple, it might provide a very useful alternative to the existing synthetic schemes for metal sulfides.

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