This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A macrocycle-assisted nanoparticulation process for bulk Ag$_2$S \^\text{†\dagger}

Xin He,\textsuperscript{a} Yuechao Wang,\textsuperscript{b} Cai-Yan Gao,\textsuperscript{a} Hong Jiang\textsuperscript{b} and Liang Zhao\textsuperscript{*a}

We report herein a new nanoparticulation process for the bulk-to-nano transformation of Ag$_2$S by incorporating both top-down and bottom-up approaches. Bulk Ag$_2$S was dissolved in solution with the assistance of a macrocyclic ligand hexamethylazacalix[6]pyridine Py$_6$ to produce polynuclear silver sulfide cluster aggregates. All Ag-S cluster aggregates obtained in three crystalline complexes were protected by Py$_6$ macrocycles. Removing the protective Py$_6$ macrocycles by protonation led to the generation of unconventional Ag-S nanoparticles with a large gap energy. Theoretical calculation by hybrid DFT method demonstrated that the silver-sulfide clusters with high Ag/S ratio exhibited more localized HOMO-LUMO orbitals, which consequently enlarged their band gap energies. These experimental and theoretical studies broaden our comprehension on the fabrication of nanomaterials by virtue of the advantages of both bottom-up and top-down methods and meanwhile provide a viable means of adjusting the band gap of binary nanomaterials independent of their size.

Introduction

Silver sulfide, a type of direct and well-known narrow band gap semiconductor,\textsuperscript{1} has attracted considerable attention due to its good stability, low toxicity\textsuperscript{2} and extensive potential applications in photovoltaic cells, photoconductors,\textsuperscript{3} infrared detectors\textsuperscript{4} and near-infrared imaging.\textsuperscript{5} Besides a band gap of 0.9-1.1 eV for bulk $\alpha$-Ag$_2$S,\textsuperscript{6} diminishing the size of Ag$_2$S to a nano-sized scale provides an efficient way to finely tune the band gap of this material based on the quantum confinement effect, thus resulting in many intriguing size-specific optical and optoelectronic properties.\textsuperscript{7} In this regard, different synthetic methods\textsuperscript{6} e.g. microemulsion approach,\textsuperscript{8} hot injection method\textsuperscript{9} etc. have been comprehensively explored during the past two decades with an aim at achieving uniformly sized Ag$_2$S nanocrystals. However, the use of exotic ligand- or surfactant-stabilized silver and sulfide ions or their precursors and the requirement of elevated temperature and high pressure in most cases made these methods an arduous synthetic protocol. Obviously, if bulk Ag$_2$S solid can be directly transformed into its nano-sized prototype, it will be a concise and ideal synthetic strategy. However, to the best of our knowledge, no reported method for the synthesis of silver chalcogenide nanomaterials involves such kind of direct transformation.

Recently, the synthesis of silver chalcogenide nanocluster compounds in crystalline form has been reported in literatures.\textsuperscript{10,11} During the reaction between various silver thiolates (SR) and silylated sulfide sources in the presence of coordinative phosphane ligands, nanometer-sized Ag/S/SR silver clusters can be generated at room temperature, but amorphous Ag$_2$S would be obtained if increasing the reaction temperature. Such biased reaction pathways suggest a possible intermediate role of silver-sulfide clusters in the synthesis of silver sulfide nano-objects. Inspired by this understanding, we envision that successful transformation of bulk Ag$_2$S to silver sulfide nanomaterials could be initiated with the synthesis of polynuclear silver sulfide cluster directly from bulk Ag$_2$S. Combination of top-down (from bulk Ag$_2$S to silver sulfide clusters) and bottom-up (from silver sulfide clusters to nanomaterials) approaches may facilitate the bulk-to-nano transformation of Ag$_2$S. However, bulk Ag$_2$S is known for its very poor solubility ($K_{sp} = 8\times10^{-51}$ at 25 ºC), which makes it a formidable challenge to dissolve bulk Ag$_2$S solid and complete the bulk-to-nano transformation by means of cluster intermediates. Very recently, we explored that a new class of
macrocycles, azacalix[n]pyridines (Py[n]), exhibited a positive allosteric effect upon binding with metal ions,\textsuperscript{12} which largely enhanced their affinity to a multimetallic aggregate and led to the formation of silver acetylide clusters by using slightly soluble polymeric [RC≡C] \textsubscript{m}. As starting materials,\textsuperscript{13} We thus conceive a synthetic strategy to implement the bulk-to-nano transformation of silver sulfide as illustrated in Scheme 1. A particular polypyridine macrocyclic ligand Py[n] will be used to facilitate the formation of macrocycle-protected silver sulfide clusters based on its positive allosteric effect at first. Upon interrupting coordination bonds between polypyridine ligands and silver atoms via protonation, the encapsulated silver sulfide clusters may mutually coalesce to finally produce silver sulfide nanoparticles, which can be stabilized by additional surfactants.

Results and discussion

Considering the high efficiency of Py[6] (composed of six 1,3-pyridine rings bridged by six N-CH\textsubscript{2} moieties)\textsuperscript{13b} in our previous synthesis of silver ethylenediide cluster-encapsulated supramolecular capsule,\textsuperscript{13b} we firstly attempted to utilize this macrocyclic ligand to dissolve Ag\textsubscript{2}S solid. When Ag\textsubscript{2}S solid was added into a methanol solution of AgCF\textsubscript{3}SO\textsubscript{3} (0.2M), no obvious color change of the solution was observed. However, addition of Py[6] into the Ag\textsubscript{2}S-AgCF\textsubscript{3}SO\textsubscript{3} mixture led to the appearance of yellow color very quickly and the gradual decrease of the Ag\textsubscript{2}S solid, suggesting the dissolution of Ag\textsubscript{2}S into the solution. It should be noticed that silver triflate is essential for dissolving Ag\textsubscript{2}S solid since only mixing Ag\textsubscript{2}S with silver triflate clarified that the species A was actually derived from the assembly of silver triflate and Py[6] due to identical proton NMR spectra (see Fig. S1 in the Supporting Information). Single crystals of the species A (denoted as crystalline complex 1) for X-ray crystallography analysis were deposited from the CH\textsubscript{2}OH/CH\textsubscript{3}Cl\textsubscript{2} mixed solution of Py[6] and AgCF\textsubscript{3}SO\textsubscript{3}. As shown in Fig. 2a, the ratio of silver triflate to Py[6] in complex 1 was determined as 3:1, giving the formula of 1 as \{Ag\textsubscript{5}(Py[6])(CF\textsubscript{3}SO\textsubscript{3})\文本{3}(H\textsubscript{2}O)\textsubscript{0.5}\}. A central silver atom Ag1 in 1 adopted a linear coordination geometry to bind with two opposite pyridines of the Py[6], thus causing the formation of a cage-like structure. This unimolecular folding fashion is similar with our previously reported scenarios for two larger macrocycles Py[8] and Py[9].\textsuperscript{14}

The structural analysis of the species B was complicated. High-resolution mass spectroscopy (HR-MS) of the Ag\textsubscript{2}S-AgCF\textsubscript{3}SO\textsubscript{3}-Py[6] yellow reaction mixture revealed two isotopically well-resolved peaks at m/z = 1258.9341 and 554.9862 corresponding to the \{[CF\textsubscript{3}SO\textsubscript{3}]\textsubscript{2}Ag\textsubscript{2}Ag(Py[6])\} and \{[CF\textsubscript{3}SO\textsubscript{3}]\textsubscript{2}Ag\textsubscript{2}(Py[6])\} species (Fig. S2), confirming the existence of the species A. In addition, several peaks corresponding to the species of a macrocycle and a polynuclear silver-sulfide cluster plus some silver triflate groups have been found as well in HR-MS (Fig. S2). For example, a strong peak at m/z = 1762.5754 can be ascribed to the species \{Ag\textsubscript{5}S\textsubscript{2}(Py[6])(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}\} and the peak at m/z = 934.7313 is isotopically in good agreement with the species \{Ag\textsubscript{6}(Py[6])(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}\}. We then conducted a crystallization process on this reaction mixture by adding diethyl ether and a crystalline compound with the formula of \{Ag\textsubscript{6}S\textsubscript{2}(Py[6])(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}\} was finally obtained. Crystal structure of 2 (Fig. 2b) comprises a central sulfur anion that is encompassed by six silver atoms while two of them (Ag5 and Ag6) each has an occupancy ratio of 0.5. This silver-sulfide cluster should be properly described as a \[Ag\textsubscript{5}-S\] aggregate, which is coordinated by a Py[6] macrocycle at one side and is further bonded by three silver triflate anions at another side. Argentophilic interactions\textsuperscript{15} and silver–aromatic π interactions both play a significant role in the stabilization of such a \[Ag\textsubscript{5}-S\] cluster situated inside a Py[6] macrocycle. Interestingly, similar crystallization process but with longer crystallization time than that for complex 2 resulted in a crystalline complex 3, which has a formula of \{Ag\textsubscript{5}S\textsubscript{2}(Py[6])(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}\} based on its crystal structure analysis. As shown in Fig. 2c, complex 3 also comprises a \[Ag\textsubscript{5}-S\] aggregate with a C\textsubscript{3}-axis symmetry, which is protected by two face-to-face Py[6] ligands to construct a cluster-embedded supramolecular capsule. To the best of our knowledge, this is the first example of a discrete silver sulfide cluster with an inner penta-coordinated sulfide.\textsuperscript{16} This \[Ag\textsubscript{5}-S\] structural motif is also consistent with the basic structural unit of bulk Ag\textsubscript{2}S.\textsuperscript{17} But in contrast, the Ag-S bond lengths in 3 (2.369(3)-2.432(4) Å) are ~0.2 Å shorter than the values in the bulk Ag\textsubscript{2}S\textsuperscript{17} and other silver-sulfide clusters.\textsuperscript{18} Another crystalline complex \{Ag\textsubscript{2}S\textsubscript{2}(Py[6])(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2}H\textsubscript{2}O(CH\textsubscript{3}OH)\} was serendipitously acquired upon reducing the amount of Py[6] applied in the above synthetic procedure for complex 2. As shown in Fig. 2d, the dumbbell-shaped \[Ag\textsubscript{2}S\textsubscript{2}\] silver-sulfide cluster aggregate in 4 can be described as two single sulfide-centered cage-
like silver clusters fused by sharing a middle silver atom. In addition, the upper and neither sides of this dumbbell-shaped silver cluster were embodied by two Py[6] macrocycles as similar as in 3. The total seven silver atoms in the asymmetric unit of 4 shared a refined site occupancy of six since silver atom Ag6 was located at a special symmetry position while Ag7 is disordered and both had a refined site-occupancy ratio less than one (see Supporting Information for details). Despite of structural difference of silver-sulfide clusters among complexes 2-4 only in nucleus and cluster configuration, the Py[6] macrocycles in 2-4 all adopted a similar quasi-C3v bowl-shaped conformation. Moreover, we substantiated that most silver-sulfide cluster species in the reaction mixture of Ag2S, AgCF3SO3 and Py[6] were stabilized by one or two Py[6] macrocyclic ligands. In addition, based on the HR-MS, 1H-NMR data and the DOSY result that reflected a size ratio (0.80) comparable to the value of 0.78 in the crystal structures of 1 and 2, we hypothesized that complex 2 that composed of a Py[6] macrocycle and a polynuclear silver-sulfide cluster is probably the second dominant species (the species B) in the reaction mixture of Ag2S, AgCF3SO3 and Py[6].

Successful isolation of discrete (in 2 and 3) and joint (in 4) silver sulfide clusters by varying the amount of the protective Py[6] proves the viability of synthesizing Ag-S binary nanoparticles through the coalescence and fusion of silver sulfide clusters. In view of the fact that Py[6] can be easily protonated by a strong acid due to the good Lewis basicity of pyridine, we then added CF3COOH into the filtrate of the reaction mixture of Ag-S, AgCF3SO3 and Py[6] to interrupt the coordination interactions between the central silver sulfide cluster and its surrounding Py[6] macrocycles. Dismantlement of Py[6] led to a clear yellow solution. This solution sample remained its yellow color within an hour, but further standing would result in a black precipitate. Formation and stepwise growth of metal sulfide nanoparticles were affirmed by transmission electron microscopy (TEM) photographs prepared at different intervals (Fig. 3a-b). We subsequently employed oleic amine7 as a surfactant to stabilize the acquired nanoparticles. The resulting yellow solution can retain its solution homogeneity for several days. TEM images of this solution sample (denoted as D-NP) substantiated the formation of metal nanoparticles with an average diameter of 4±0.4 nm (Fig. 3c). Fourier transform IR spectroscopy analysis of the solid sample of D-NP prepared by centrifugation clearly showed the absence of Py[6] and the existence of oleic amine molecules in D-NP (Fig. S3). This observation verified our above assumption that Py[6]-protected silver sulfide clusters could indeed undergo a deprotection process to act as nuclei and activated monomers for the fabrication of silver sulfide nanoparticles. Notably, we found that the acidified Py[6] ligands can be recycled after neutralization and extraction and then employed for subsequent bulk-to-nano transformation of silver sulfide.

Fig. 2 (a) Crystal structure of complex [Ag5(py)[6](CF3SO3)3•CH3OH]1 (1). Selected bond distances (Å): Ag1-N5 2.154(3); Ag1-N11 2.168(3); Ag2-N9 2.281(4); Ag3-N3 2.284(3). (b) Partial crystal structure of [Ag5(S(py)[6])(CF3SO3)3]•CH3OH (2). Ag5 and Ag6 each has an occupancy ratio of 0.5. The three triflate groups at top side of the [Ag5-S] cluster were omitted for clarity. Silver-aromatic π interactions were shown by dashed lines. Ag-C distances (Å): Ag1-C11 2.987; Ag1-C19 2.948; Ag2-C7 2.731; Ag2-C35 2.957; Ag3-C23 2.836; Ag3-C31 3.090. (c) Side view of complex [Ag5(S(py)[6])(CF3SO3)3] (3) with the central silver-sulfide cluster presented by a polyhedron. (d) Crystal structure of [Ag5,S(py)[6](CF3SO3)3•2H2O•CH3OH]2 (4). Two silver atoms each has an occupancy ratio of 0.5. Triflate groups and solvent molecules were omitted for clarity. Color scheme for atoms: Ag, purple; C, gray; H, white; N, blue; S, yellow; F, cyan.

Fig. 3 TEM images of deprotected silver sulfide clusters after adding CF3COOH (a) 30 s and (b) 2 min later. (c) TEM images of sample D-NP, inset Size-distribution histogram of silver sulfide nanoparticles in D-NP. (d) UV-vis spectrum of D-NP in cyclohexane at 298 K.

On the other hand, high-resolution TEM (HR-TEM) of D-NP showed very ambiguous lattice fringes in contrast to the clear pattern in previously reported Ag2S nanoclusters19 suggesting a poorly crystalline form of D-NP. The low crystallinity of D-NP was further substantiated by selected area electron diffraction (SAED) (Fig. S4), which exhibited two feeble diffraction rings that could be indexed to the (-103) and (232) facets of monoclinc Ag2S (JCPDS card 14-0072). The
energy dispersive X-ray spectroscopy (EDX) of D-NP indicated the presence of element Ag and S and further offered the Ag/S atomic ratio equaling to 3.5 (Fig. S5). We also conducted the XPS experiment of D-NP. As reflected in the XPS experiment (Fig. S6), we confirmed the +1 oxidation state of the silver atoms in D-NP based on their Ag 3d$^{10}$ and Ag 3d$^{11}$ binding energy peaks at 374.5 and 368.5 eV. In addition, the Ag/S molar ratio was determined as 3.7 based on the XPS data, which is comparable to the energy dispersive X-ray spectroscopy (EDX) data of 3.5. This Ag/S elemental ratio in D-NP is larger than the values of around 2.0 in bulk Ag$_2$S$^{17}$ and previously reported silver sulfide nanoclusters$^{13,19}$. We hypothesized that such high Ag/S ratio in D-NP may arise from the coalescence and fusion of the silver-rich Ag-S clusters in 2-4 by forming inter-cluster interactions (e.g., argentophilicity) and sharing silver atoms as similar as the above-mentioned scenarios in 2-4. In addition, the absorption spectrum of the cyclohexane solution of D-NP (Fig. 3d) exhibited a monotonic decrease in the whole recorded range, which is similar to the spectra of a number of reported silver sulfide nanocluster samples.$^{20}$ The band gap energy could be fitted by using the Bardeen or Tauc equation (Fig. S7). Direct transitions of D-NP was thus deducted to be 4.0 eV, largely blue-shifting relative to the band gap of the bulk α-Ag$_2$S.$^{7}$ It is noteworthy that modifying the composition ratio of different constituents in nanomaterials in order to perform band gap adjustment has been frequently applied in ternary and quaternary alloyed semiconductor nanomaterials, but rarely in binary systems.$^{21}$ The method reported herein represents a viable means to tune the band gap of binary nanomaterials independent of their size.

Conclusions

In summary, we have demonstrated a viable means of synthesizing silver sulfide nanomaterials directly from its bulk form in terms of the assistance of coordinative macrocyclic ligands. This method could be successfully applied in the fabrication of other binary silver nanomaterials such as silver halides, acetylides etc. based on our recent investigation. Considering the size of macrocyclic ligands can dominate the nuclearity number of acquired metal cluster aggregates, this approach can also be employed to achieve nanomaterials with different properties dependent on different nucleation centers. This study foresees the synthesis of numerous new nanomaterials with novel properties based on their synthetic revisiting inspired by the combination of bottom-up and top-down methods reported herein.

Acknowledgements

Financial support by the MOST (973 program, 2013CB834501 and 2011CB932501) and NNSFC (91127006, 21132005, 21121004) is gratefully acknowledged. This work is also supported by MOE (NCET-12-0296), Tsinghua University Initiative Scientific Research Program (2011Z02155) and Beijing Higher Education Young Elite Teacher Project (YETP0130). We are grateful to Profs. Mei-Xiang Wang and De-Xian Wang for their helpful discussion.

Notes and references

1. The Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: zhaolchem@mail.tsinghua.edu.cn.
2. Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.
4. This work is dedicated to Professor Thomas C. W. Mak in celebration of his 78th birthday.


