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## PAPER

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# Towards atomically precise luminescent Ag<sub>2</sub>S clusters separable by thin layer chromatography<sup>†</sup>

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Here, we report the synthesis of monolayer protected, luminescent and atomically precise silver sulfide  $(Aq_2S)$  clusters. Cluster formation was studied by varying the conditions of the reaction. Matrix assisted

laser desorption ionization mass spectrometry (MALDI MS) was used to monitor the growth of clusters to nanoparticles (NPs). Clusters of different nuclearity were obtained at a lower temperature, and were

efficiently separated by thin layer chromatography (TLC). One of the clusters was assigned as

Ag<sub>158</sub>S<sub>79</sub>(SBB)<sub>32</sub>, where SBB is 4-tert-butylbenzyl mercaptan.

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## Introduction

Colloidal semiconductor nanoparticles (NPs), also called quantum dots (QDs), have been considered as one of the major advances in materials science.1-3 QDs attracted intense research interest since their discovery in the 1980s due to their unique physical and chemical properties which include broad absorption, narrow emission, and negligible photobleaching.<sup>4-6</sup> Cadmium chalcogenides (CdS and CdSe) have been the most studied nanocrystals.<sup>5</sup> But toxicity of cadmium based materials is a great concern in many of their potential applications. In recent years, researchers started focusing on the less toxic silver chalcogenide systems (Ag<sub>2</sub>E, where E = S, Se).<sup>7</sup> Silver chalcogenides have a low band gap ( $\sim$  1.0, 0.15 and 0.67 eV for bulk Ag<sub>2</sub>S, Ag<sub>2</sub>Se and Ag<sub>2</sub>Te, respectively) and are active in the near-infrared (NIR) region. NIR emitting QDs have great impact in biomedical diagnostics and therapy.<sup>8</sup> Ag<sub>2</sub>S NPs with tunable emission from 690 to 1200 nm were successfully synthesized by Jiang et al.9 2-Mercaptopropionic acid (2-MPA) coated NIR emitting Ag<sub>2</sub>S were prepared by Hocaoglu et al.<sup>10</sup> The same group reported the synthesis of emission tunable cyto/hemocompatible NIR emitting Ag<sub>2</sub>S QDs by meso-2,3-dimercapto succinic acid (DMSA) decomposition.<sup>11</sup> Here DMSA acts as both the sulfur source and the protecting agent. Hong et al. showed in vivo fluorescence imaging with Ag<sub>2</sub>S quantum dots in the range of 900-1300 nm.12 Tunable visible to NIR emitting Ag<sub>2</sub>S QDs were synthesized and used for integrin targeted cancer imaging by Tang et al.13

NPs having only a few atoms have structure and properties different from NPs and bulk materials.<sup>14,15</sup> NPs of this kind are known as nanoclusters, which have to be treated differently. Synthesis of atomically precise clusters of noble metals gained great interest after the pioneering work of Brust and co-workers in 1994.16 Clusters of gold and silver are the most studied systems of which there are many examples today.<sup>14,15</sup> Many of these structures have been solved by single crystal X-ray diffraction (XRD).<sup>17-21</sup> Clusters of silver and copper chalcogenides have been studied in detail by Fuhr et al. and they have summarized this work recently.<sup>22</sup> These coinage metal chalcogenide clusters were understood mainly from their crystal structures. The inherent insolubility of these clusters in organic solvents limited their nuclear magnetic resonance (NMR) and mass spectral characterization, which are the extensively used techniques in the case of noble metal clusters.<sup>23</sup> There are a few mass spectral studies on cadmium and zinc chalcogenide clusters as well.<sup>24-26</sup>

Nanoclusters of different materials find applications in various fields like sensing, catalysis, bioimaging, *etc.* owing to their unique chemical and physical properties. In order to understand the unique optical and luminescence properties, pure materials are essential. Some of the synthetic methods result in differently sized clusters, which need further separation. Different methods like high-pressure liquid chromatography (HPLC), polyacrylamide gel electrophoresis (PAGE), solvent extraction, and thin layer chromatography (TLC) have been used for cluster separation.<sup>27–31</sup> Recently gel permeation chromatography was used for the separation of indium phosphide (InP) clusters from InP QDs.<sup>32</sup>

In this report, we describe the synthesis of highly soluble monolayer protected silver sulfide clusters. The influence of temperature of synthesis on the optical properties of the prepared clusters was studied. Cluster formation was investigated using mass spectrometry. Monodisperse clusters were obtained by tuning

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: MALDI MS of solvent dependent cluster synthesis, MALDI MS of Ag<sub>2</sub>S-70 and TLC separated Ag<sub>2</sub>S-70, ESI MS of Ag<sub>2</sub>S-60 and TLC separated clusters, TEM images of TLC separated Ag<sub>2</sub>S-60 and EDS spectrum of Ag<sub>2</sub>S-80 cluster. See DOI: 10.1039/c7tc05858f

## **Experimental section**

#### Materials and methods

All the chemicals used were commercially available and were used without further purification. Silver acetate (CH<sub>3</sub>COOAg, 99.99%), sulfur powder (100 mesh 99.5%), octadecene (ODE, technical grade, 90%), oleyl amine (OA, technical grade, 70%) and 4-*tert*-butylbenzyl mercaptan (BBSH) were obtained from Sigma Aldrich, India. Toluene (99.5%) and tetrahydrofuran (THF, 99.5%) were purchased from Merck, India, and methanol (99.5%) was from Finar, India.

#### Synthesis of cluster

Silver sulfide clusters were synthesized by a reported method used for the synthesis of mixed silver chalcogenide clusters.<sup>33</sup> About 0.1 mmol silver acetate and 4 mmol BBSH were taken in a three necked round bottom flask containing 5 ml ODE. This mixture was stirred for 1 h at 60 °C under continuous Ar purging followed by the addition of 0.05 mmol of sulfur powder to the mixture and it was stirred for 2 h. Then the reaction mixture was cooled to room temperature and the cluster was purified by methanol precipitation and centrifugation. The purified cluster was soluble in toluene, THF, DCM, DMF, *etc.* Clusters in toluene were used for further studies. Different clusters were synthesized by changing the temperature at which sulfur was added such as 70, 80 and 90 °C.

#### **TLC** experiment

 $3 \mu$ l of cluster samples were pipetted to the TLC plate and dried in air. After drying, the plate was eluted with THF/MeOH mixture. After the separation, the bands were cut from the TLC plate and extracted in THF.

#### Instrumentation

Absorbance spectra were measured using a PerkinElmer Lambda 25 instrument in the range of 200-1100 nm. Matrix assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Biospectrometry Workstation from Applied Biosystems. A pulsed nitrogen laser of 337 nm was used for MALDI MS studies. Mass spectrum was collected in both positive and negative ion modes. The matrix used was DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile). High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 3010 (JEOL Ltd) instrument. The sample dissolved in toluene was drop casted on a carbon coated copper grid, dried at room temperature and was used for TEM measurements. Jobin Yvon NanoLog instrument was used for photoluminescence measurements. Thermogravimetric (TG) analyses were carried out on a PerkinElmer TGA7 instrument. FEI quanta 200 scanning electron microscope fitted with a tungsten filament was used for energy dispersive spectroscopy (EDS) measurements. All electrospray ionization mass spectrometric (ESI MS) measurements were performed in an ion trap LTQ XL mass spectrometer of Thermo Scientific, San Jose, CA, USA. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Omicron ESCA probe spectrometer with polychromatic Mg K $\alpha$  X-rays ( $h\nu$  = 1253.6 eV).

### Results and discussion

A single step procedure was followed for the synthesis of  $Ag_2S$  clusters (Scheme 1). In a typical reaction, silver formed yellow silver thiolate with BBSH. After the addition of sulfur powder, the solution turned brownish, which was the result of the formation of  $Ag_2S$ . Properties and particle size of silver sulfide clusters can be tuned by different parameters such as temperature, silver:ligand and silver:sulfur ratios. Here cluster growth was studied by changing the temperature of the reaction as this is the most important parameter affecting crystal growth and properties of the resultant material.<sup>10,11</sup> Sulfur was added to the reaction mixture at 60, 70, 80 and 90 °C. The clusters synthesized at different temperatures are denoted as  $Ag_2S$ -60,  $Ag_2S$ -70,  $Ag_2S$ -80, and  $Ag_2S$ -90 hereafter.

Monolayer protected clusters are understood largely by mass spectrometry, which gives the atomic composition of the cluster. Molecular understanding of noble metal clusters is well known in the literature, whereas similar studies on semiconductor ODs are very few. Earlier reported MALDI MS of silver chalcogenide clusters showed a series of peaks in the higher mass region, along with the molecular ion peaks. This observation was explained in terms of the aggregation of clusters, after desorption of the SR group.<sup>34,35</sup> MALDI MS spectra of the clusters observed here are shown in Fig. 1 (full range MALDI MS spectra is shown in Fig. S1, ESI<sup>+</sup>). In this case, we did not observe similar kinds of cluster aggregation in MALDI MS. Only specific peaks were seen. Reactions at 60 and 70 °C gave a mixture of clusters in the range of 20 and 25.5 kDa (Fig. 1 orange and violet). When the temperature of the reaction was 60 °C, intensity of the 20 kDa cluster was higher. The peak at 25.5 kDa started increasing when the temperature of the reaction was raised to 70 °C. The appearance of two peaks in the MALDI MS was not due to cluster aggregation and will be explained later in the paper. A single mass species was obtained when the temperature of the reaction was increased to 80 °C (Fig. 1 pink trace). Further increase in temperature gave bigger NPs, which were not ionizable in MALDI (cyan trace). It was observed that the medium of synthesis also plays a significant role in cluster formation (Fig. S2, ESI<sup>+</sup>). Cluster synthesis was performed in different solvents like ODE,



Scheme 1 Scheme used for the synthesis of BBSH protected luminescent silver sulfide clusters.



Fig. 1 MALDI MS spectrum of  $Ag_2S$  clusters synthesized at different temperatures (temperatures shown on the right). Inset shows the visible light photograph of the same.

toluene, and OA at 80  $^{\circ}$ C (at this temperature only a single product forms). While ODE gave a single product, toluene gave clusters with different nuclearity. In the case of OA, no cluster formation was observed, rather it resulted in NPs.

Absorption and emission properties of these clusters were studied to understand the effect of temperature on the particle size (Fig. 2). Ag<sub>2</sub>S-60 showed a broad absorption around 660 nm. In the case of Ag<sub>2</sub>S-70, the absorption was red shifted to 740 nm. As we increased the reaction temperature further, prominent absorption features were not observed. The photoluminescence spectrum of Ag<sub>2</sub>S-60 and Ag<sub>2</sub>S-70 showed two emission features one in the visible ( $\lambda_{ex} = 600$  nm) and another in the NIR ( $\lambda_{ex} = 700$  nm) region, which are due to mixed clusters. The 25.5 kDa cluster synthesized at 80 °C showed a NIR emission around 1020 nm ( $\lambda_{ex} = 700$  nm). Ag<sub>2</sub>S-90 NPs emitted around 1080 nm ( $\lambda_{ex} = 700$  nm). Seemingly the higher



Fig. 2 Temperature dependent UV-vis and photoluminescence spectra of Ag<sub>2</sub>S clusters. UV-vis and photoluminescence spectra of Ag<sub>2</sub>S-60, Ag<sub>2</sub>S-70, Ag<sub>2</sub>S-80 and Ag<sub>2</sub>S-90 clusters are given in orange, violet, pink and cyan traces respectively. Two detectors were used for measuring the PL data of the sample. In the first detector (Detector 1), the intensity falls down drastically above 800 nm due to the poor efficiency of this detector above this wavelength. The second detector (Detector 2) is sensitive only in the 850–1450 nm window.

temperature synthesis shows only one major emission due to one cluster and the low temperature synthesis shows two emission due to two clusters, which agreement with the mass spectra.

TLC has been shown as an efficient and simple technique for the separation of atomically precise gold clusters.<sup>30,31</sup> Here, we show the separation of mixed Ag<sub>2</sub>S clusters using TLC. Good separation was achieved using THF/methanol mixture (80:20) as the solvent (Fig. 3). Choice of solvent was important in the case of separation. When eluted with 100% THF, whole sample moved with the solvent front. The addition of proper ratio of methanol separated the cluster. An optical photograph of the TLC plate used for separation is shown in Fig. 3. The two bands were cut from the TLC plate and the bands were extracted by THF and used for characterization. MALDI MS was measured using the extracted sample which showed a single peak for individual bands (Fig. 3). Band one was the larger 25.5 kDa cluster and band two was the smaller 20 kDa cluster. As expected, the heavier cluster moved only a shorter length on the TLC plate. The TLC purified clusters were showing a peak representing the dimers of the cluster in MALDI MS. Similarly Ag<sub>2</sub>S-70 cluster was also separated by TLC (Fig. S3, ESI<sup>+</sup>).

ESI MS of the cluster was measured for understanding the exact composition of the synthesized clusters. The clusters synthesized in this process were neutral leading to difficulty in ionization in ESI.<sup>†</sup> Ionization enhancers like cesium acetate were also used for enhancing the possibility of ionization. After the addition of ionization enhancers, we could observe some cluster fragments



Fig. 3 TLC separation of Ag<sub>2</sub>S-60 clusters. MALDI MS data of the parent sample (orange trace) and TLC separated clusters (violet trace shows a peak at 25.5 kDa is due to band one and pink trace shows a peak at 20 kDa is due to band two) confirming the separation by TLC. Optical photograph of the TLC plate used for the separation. Slight overlap of TLC bands resulted in a weak 25.5 kDa peak in the spectrum of band two. Some of the parent cluster get adsorbed strongly at the TLC plate and are not extractable are shown as a spot at the base.

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**Fig. 4** (A) Comparative UV-vis spectra of parent (orange trace) and TLC separated (violet trace for band one and pink trace for band two)  $Ag_2S-60$  clusters. (B) Jacobian corrected absorption spectra of different clusters synthesized. Inset shows the expanded spectra for band gap determination. (C) Jacobian corrected absorption spectra of the parent and TLC separated  $Ag_2S-60$  clusters are compared. Spectra is expanded in the set for band gap calculation. (D) Photoluminescence spectra of parent and TLC separated clusters are compared. TLC band one was of a bigger cluster emitting in the NIR region. Band two was of smaller 20 kDa cluster which showed emission in the visible region. The sudden decrease in intensity above 800 nm for band one in the visible region is due to the poor detector efficiency in this window.

in the positive ion mode (Fig. S4, ESI<sup>†</sup>). Same fragment peaks were seen in the TLC separated clusters indicating that these are fragments of the cluster.

Ag<sub>2</sub>S is a narrow band gap semiconductor having a band gap of 0.9 eV. UV-vis spectra of parent clusters and those of separated bands are shown in Fig. 4A. The synthesized clusters showed a larger band gap compared to the bulk. Fig. 4B shows a comparative absorption spectra of these clusters plotted in terms of energy. This plot is obtained by doing the Jacobian correction (see ESI<sup>†</sup>).<sup>14</sup> Fig. 4C shows the Jacobian corrected plot for parent and TLC separated clusters. Extrapolation of the linear region of the energy plot to the horizontal axis gives the band gap of the synthesized clusters. Ag<sub>2</sub>S-60, -70, -80 and -90 showed band gap values 1.33, 1.18, 1.08 and 1.00 eV respectively. TLC separated Ag<sub>2</sub>S-60 clusters showed small change in band gap (Fig. 4C). Band one was 1.32 and band two was 1.36 eV. It was shown that the parent cluster has two emission peaks (Fig. 2). The bands collected after TLC gave single emission bands (Fig. 4D).

TEM images of these clusters showed mixed particle distribution for  $Ag_2S-60$  (Fig. 5A) and  $Ag_2S-70$  (Fig. 5B). In Fig. 5A and B different cluster populations are marked red circles for larger and yellow circles for smaller clusters. Monodisperse particles were seen in the case of  $Ag_2S$ -80, which is in good agreement with the presence of single peak in MALDI MS (Fig. 5C).  $Ag_2S$  particles of 5 nm size were formed at 90 °C (Fig. 5D). HRTEM image of one particle is shown in the inset of Fig. 5D. TEM images of TLC separated clusters are shown in Fig. S5 (ESI<sup>†</sup>).

XPS analysis was performed to confirm the elemental composition of the cluster. Survey spectra showed the presence of silver and sulfur. Silver binding energy was matching with the reported values of monovalent silver. Ag<sub>2</sub>S-60 parent cluster, TLC separated band 1 and band 2 showed Ag  $3d_{5/2}$  binding energies at 368.2, 368.4, and 368.3 eV and Ag  $3d_{3/2}$  binding energies at 374.3, 374.4, and 374.2 eV, respectively (Fig. 6A). Binding energy values were 162.1, 162.1, and 161.8 eV respectively for S  $2p_{3/2}$  and 163.4, 163.3, and 162.9 eV, respectively for S  $2p_{1/2}$ , for the above mentioned samples (Fig. 6B). These values are comparable to those of sulfide (S<sup>2-</sup>) species.

Thermogravimetric analysis of the Ag<sub>2</sub>S-80 cluster was performed under nitrogen atmosphere. TG curve shows 23% weight loss, which is expected to be due to the organic ligand



**Fig. 5** TEM images of Ag<sub>2</sub>S-60 (A), Ag<sub>2</sub>S-70 (B), Ag<sub>2</sub>S-80 (C), and Ag<sub>2</sub>S-90 (D). In image (A) and (B), mixed clusters are marked by red (big) and yellow (small) circles. Image (C) is more uniform in size. Ag<sub>2</sub>S-90 (image D) is of bigger nanoparticles, which are not observable in MALDI MS. HRTEM image of one particle is given in the inset of D. Lattice spacing of 0.24 nm is marked, which is the  $d_{(112)}$  plane of Ag<sub>2</sub>S. Particle distribution for each sample is shown in each TEM image. Particle distribution was obtained by expanding the image and counting manually.

desorption (Fig. S6, ESI<sup>†</sup>). This means that 23% of the 25.45 kDa mass is due to the SBB ligand. The remaining mass is attributed to the Ag<sub>2</sub>S core. It is also likely that the ligand can desorb as R–S–R, R–S–S–R or R–R. However, most of the desorption in thiolate protected clusters is seen as R–S–S–R.<sup>36,37</sup> Absence of molecular ion peaks in the ESI MS made the assignment of a molecular formula difficult. The mass loss of 23% in a 25.45 kDa cluster is 5854 Da. Therefore, the number of ligands can be

calculated by dividing this mass by thiol mass, which is 179.41. This suggest that there can be ~32 ligands in the clusters. The remaining mass of 19569 Da (after substracting mass due to thiol) is due to the Ag–S core and this can contain ~79 Ag<sub>2</sub>S units. The molecular composition can be inferred based on the factors such as the mass of the molecular ion, core size, *etc.* With the ligand loss determined from the TG, the total molecular formula may be given as  $Ag_{158}S_{79}(SBB)_{32}$ . This is in agreement with the observed Ag:S ratio of 1:0.65 (Fig. S7, ESI†). A cluster of this kind having a nuclearity of  $Ag_{158}S_{79}(SBB)_{32}$  accounts for all the experimental data.

## Summary

In conclusion, we synthesized a series of monolayer protected Ag<sub>2</sub>S clusters. These clusters were highly soluble in organic solvents, which made the evaluation of solution phase properties possible. Clusters showed quantum confinement. Reactions at 60 °C and 70 °C gave a mixture of 20 kDa and 25.5 kDa clusters. Monodisperse 25.5 kDa clusters were obtained at 80 °C. These clusters were separated by simple thin layer chromatography. The separated clusters were soluble in common organic solvents. A tentative composition was proposed for one such cluster based on various analytical data.

## Conflicts of interest

There are no conflicts to declare.

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Fig. 6 XPS spectra Ag<sub>2</sub>S-60 parent cluster and TLC separated clusters. (A) Specific regions of Ag (A) and S (B). Appropriate background substraction and peak fitting have been performed.

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