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Highly luminescent monolayer protected Ag₅₆Se₁₃S₁₅ clusters[†]

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A highly luminescent (quantum yield 21%) mixed chalcogenide silver cluster, $Ag_{56}Se_{13}S_{15}$ cluster of Ag_2X stoichiometry, protected with a 4-*tert*-butylbenzyl mercaptan ligand has been synthesized and characterized. Investigation using diverse tools of analysis such as mass spectrometry, elemental analysis, thermogravimetry and X-ray diffraction confirmed this composition. The cluster emits in solution and in the solid state and has been deposited on oxide supports to get red emitting films. The specificity of cluster emission to the mercuric ion Hg(II), among a range of heavy metal ions, was used to develop a sensor, which shows sensitivity down to 1 ppb. A pH paper like visual detector was developed by combining the Hg(II)-sensitive emission of the cluster and the insensitive emission of fluorescein isothiocyanate. The test strip showed visual detection down to 1 ppb in real water samples.

Introduction

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Semiconductor quantum dots (QDs) have been the subject of rigorous investigations for the last 25 years.¹ Chalcogenides of cadmium (Cd) have been the main interest in these studies, which expanded into almost all areas of chemistry, physics and biology, largely because of their unusual photophysical properties.^{2–4} Concerns about toxicity encouraged investigation of other chalcogenides which have reduced cytotoxic effects. Silver (Ag) chalcogenides have also been examined because of their lesser toxicity.^{5,6} Emission of Ag_2E QDs [E = sulfur (S), selenium (Se)] is extensive, from visible to near infrared (NIR), although their quantum yields (QY) have not been as large as the analogous CdE systems. Silver sulfide (Ag₂S) nanocrystals with a tunable NIR emission ranging from 690-1227 nm have been reported by Jiang et al.⁷ Tan et al. studied ultraviolet (UV) or visible light irradiation on nitric oxide (NO) release from s-nitrosothiol conjugated glutathione protected Ag₂S QDs.⁸ Tan et al. also used Ag₂S chitosan nanospheres for NIR fluorescence imaging.9 NIR emitting silver selenide (Ag₂Se) QDs have also been reported by different groups.¹⁰ Temperature dependent photoluminescence (PL) of Ag₂Se QDs were studied by Ji et al.¹¹

Well defined nanoscale molecules of M_2E systems M = Ag, copper (Cu)] with phosphine and thiolate protections were studied by Fuhr et al. and a recent summary of such research is highly informative.¹² These studies were mainly focused on the synthesis and structural characterization, from which a wide variety of structural motifs have been discovered. However, PL and related applications of these materials have rarely been explored. One of the examples where such studies have occurred is $Ag_{62}S_{13}(StBu)_{32}^{4+}$ where an emission at 613 nm with a QY of 0.014 was seen.¹³ This molecule was crystallized and its structure has been determined using single crystal X-ray diffraction (XRD). There remains a possibility of creating mixed chalcogenide systems such as $Ag_2S_{1-x}Se_x$ with varying compositions and tunable properties. With appropriate ligand protection, these nanosystems could be used for diverse applications. Anion substitution in QDs has been used to create materials with varying properties (for example, $CdS_{1-r}Se_r$). It is also known that substitution of Se into Ag₂S retains the monoclinic phase up to the composition, $Ag_2S_{1-x}Se_x$ with $0 \le x \le 0.6$ and a orthorhombic phase appears only above $0.8 \le x \le 1$.¹⁴ This suggests retention of the acanthite phase in $Ag_2S_{1-x}Se_x$ nanoparticles (NPs) for a considerable range of stoichiometry, thus allowing structural characterization.

Over the years there have been intense efforts to make atomically precise clusters of many materials. Most of the advances in this area have been centered on the noble metal clusters of which there are many examples available today.^{15–18} Some of the clusters have been crystallized and their structures have been determined by X-ray crystallography.^{19–22} These clusters possess unique structural motifs as well as diverse chemical interactions. Whereas properties of isolated clusters in solution have been explored in detail, the properties of the crystals are not understood all that well. Clusters of other

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elements have been rare, examples include those of silicon, germanium and so on. Among these compounds, the chalcogenide clusters have been explored in greater detail. These include the Ag-Se/S systems and the Cu-Se/S systems. Most such studies in this area were focused on structure and less commonly on their properties. Such materials in the nanometer regime can also be characterized using mass spectrometry (MS). Mass spectrometry has been used extensively for the characterization of noble metal clusters,²³ known as aspicules.²⁴ Several clusters in this category are known, such as Au₂₅SR₁₈, which exhibit unique properties and reviews on them are available elsewhere.²⁵ Success of such characterization depends on the ability to form stable ions in the gas phase. The inherent electronic stability of noble metals and the stability of the metal thiol interface made characterization of Au-SR clusters easier. For chalcogenides, inherent instability of the system made MS examination difficult. The Ag-Se bond (bond energy of 202 kJ mol⁻¹) is weaker than the Ag–S bond (bond energy of 217.1 kJ mol⁻¹), which made further MS investigation of Ag₂Se challenging.

Combining the distinct possibility of making a ligated $Ag_2S_{1-x}Se_x$ system and incorporating the lessons from the aspicule work, it was thought to be worthwhile to explore the mixed silver chalcogenide cluster. In this paper, the synthesis of such a mixed cluster system, tentatively assigned as $Ag_{56}S_{15}Se_{13}$ @SBB₂₈ with distinct red emission, high QY (21%) and exhibiting useful sensing properties both in solution and in the solid state is presented. Another reason to explore such a cluster system was because of the possibility of conducting experiments under milder conditions than typically used for the synthesis of Ag_2Se NPs. The standard approach used for Ag_2Se NPs and Ag-SR clusters was combined to achieve the present experimental methodology.

Experimental section

Materials and methods

All chemicals were commercially available and used without further purification. Silver acetate (CH₃COOAg), Se powder (100 mesh, 99.5%), octadecene (ODE, 90%) and 4-*tert*-butylbenzyl mercaptan (BBSH) were purchased from Sigma-Aldrich. Toluene was obtained from Merck (India) and methanol from Finar Chemicals (India).

Synthesis of luminescent cluster

Ag₂Se clusters were synthesized using a low temperature method. CH₃COOAg (0.1 mmol) and of BBSH (4 mmol) were added to 5 ml of ODE in a 100 ml three necked round bottomed flask under an argon (Ar) flow at 60 °C. Ar purging was continued for 30 min at this temperature. Then the reaction mixture was heated to 90 °C. Se powder (0.05 mmol) was added to this mixture under constant stirring and the reaction was continued for 2 h. The reaction mixture was then cooled to room temperature and purified by washing with methanol and subsequent centrifugation. The methanol precipitated cluster was re-dispersed in toluene and was used for further studies. The cluster was found to be soluble

Sensing experiment

A thin layer chromatography (TLC) plate was coated with the cluster, which was prepared by dipping the TLC plate in cluster solution for 10 minutes and then drying it in air. Cluster adsorption on the TLC was evident from the intense lumines-cence obtained under UV light.

Instrumentation

Ultraviolet-visible (UV-Vis) spectra were measured with a PerkinElmer Lambda 25 instrument in the range of 200-1100 nm. Fourier-transform infrared spectra were measured with a PerkinElmer Spectrum One instrument. Matrix-assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using an Applied Biosystems Voyager-DE PRO Biospectrometry Workstation. A pulsed nitrogen laser at 337 nm was used for the MALDI MS studies. Mass spectra were collected in both the positive and negative ion modes. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile. High-resolution transmission electron microscopy (HRTEM) was performed on a Jeol 3010 ultrahigh resolution analytical electron microscope. Samples for TEM were prepared by drop casting the toluene solution of cluster on a carbon coated copper grid and drying at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an Omicron ESCA probe spectrometer with polychromatic Mg Ka X-rays ($h\nu$ = 1253.6 eV). Luminescence measurements were carried out on a Jobin Yvon NanoLog instrument. Scanning electron microscopic (SEM) images and EDAX spectra were obtained using a FEI Quanta 200 SEM. Thermogravimetric analysis (TGA) measurements were obtained using PerkinElmer TGA7, and TA Instruments O500 Hi-Res TGA instruments. Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 Advance X-ray diffractometer.

Results and discussion

Highly luminescent Ag_2Se clusters were synthesized by the addition of Se powder to the yellowish silver thiolate at 90 °C. The purified clusters were red in color and the corresponding optical absorption spectrum showed three prominent peaks, centered at 370 nm (3.35 eV), 445 nm (2.78 eV) and 570 nm (2.17 eV) which are different from those of the Ag_2Se and Ag_2S NPs reported so far. This cluster showed intense red luminescence under UV light both in the solution state and in the solid state (inset of Fig. 1) with a strong emission peak maximum around 625 nm (Fig. 1c). Previously reported Ag_2Se and Ag_2S NPs showed UV-Vis absorption in the higher wavelength region (above 600 nm). Most of the silver chalcogenide QDs have NIR emission and these emissions are highly size dependent. The PL QY of the cluster was calculated to be 21% using Rhodamine 6G as reference (QY = 94% in water). This QY is much higher



Fig. 1 Comparison of UV-Vis spectrum (a), excitation spectrum (b) and emission spectrum (c) of the cluster solution. Axis on the right is for traces (b) and (c). The cluster solution shows a strong emission around 625 nm with three excitation maxima (359, 440 and 564 nm), all of which resulted in a single emission maximum. The inset shows the photograph of the cluster under visible and UV light in solution state (1,1') and solid state (2,2'), respectively.



Fig. 2 MALDI MS of the purified cluster measured at threshold laser power in negative mode showing a single peak around 12.5 kDa. TEM images of the cluster showing highly monodispersed particles is shown in the inset (a). Inverse fast Fourier transform result of the same image is shown in (b).

than the already reported values of organic soluble noble metal clusters and other silver chalcogenide QDs.

Mass spectrometry is the best tool to assign such clusters precisely.^{26,27} This technique is being used extensively for noble metal clusters. Molecular understanding of QDs using MALDI MS is very rare.^{28–32} A sharp peak centered at 12.5 kDa was seen in the negative mode of MALDI MS (Fig. 2). Absence of other higher mass peaks in the mass spectra confirms the formation of small clusters unlike the other QDs where a series of peaks are typically seen. TEM images showed high monodispersity of the cluster with an average particle size of ~ 2 nm (inset of Fig. 2). Interestingly, these clusters assembled themselves in a hexagonal pattern throughout the TEM grid.

Identification of molecular mass and high monodispersity are not enough to calculate the precise composition of such clusters because the MALDI MS spectrum is broad, in comparison to monolayer aspicules such as Ag152.²⁷ For further understanding of the composition, TGA was done and the corresponding data are presented in Fig. 3A. The TGA data suggest 40% weight loss around 250 °C which corresponds to the organic content present in the thiol functionality and the core mass may be calculated based on this. The cluster shows a typical PXRD pattern as shown in Fig. 3B(a). The XRD of the purified cluster showed a broad peak similar to other monolayer protected metal nanoclusters. Annealing of the cluster at 250 °C under an Ar atmosphere for 1 h gave a well defined XRD pattern which is shown in Fig. 3B(b). This XRD pattern matched with the Ag₂S acanthite phase (JCPDS No. 14-0072). The SEM EDS mapping and quantification data of the purified cluster solid showed an approximate ratio of Ag:Se:S as 1:0.24:0.70 (Fig. S1, ESI[†]). The EDAX data corresponding to the annealed cluster was also measured (Fig. S2, ESI⁺). This shows the presence of Ag, Se and S in the ratio 1:0.24:0.30. Annealing of the cluster under an inert atmosphere causes the detachment of the thiol protecting group, which is also evident from the EDAX data. A 40% weight loss in the TGA is in good agreement with the EDAX quantification. All of this quantitative data suggest that the cluster core also contains sulfur. In earlier work it has already been shown that Ag₂S NPs can form in solution above 80 °C, starting from Ag25SR18 clusters.33 The scission of the C-S bond of thiolate and release of S^{2-} have also been reported by Wang *et al.* Servotkin et al. reported that in silver sulfoselenide systems,



Fig. 3 (A) Thermogravimetric curve of the cluster. (B) XRD pattern of the cluster before (a) and after (b) annealing. XRD of the annealed clusters compared with Ag₂S JCPDS data (Black spectrum) (JCPDS No. 14-0072).

the acanthite phase is retained up to the composition, $Ag_2Se_xS_{1-x}$ with $0 \le x \le 0.6$ and the nammunite phase exists in the range of $0.8 \le x \le 1.^{14}$ Observation of an Ag_2S type XRD pattern for the cluster is in good agreement with this report (Fig. 3B). The data presented here implies the formation of a cluster of composition AgSeS(@SR. In the as-prepared condition, as it is in the cluster size regime, there are no well-defined peaks and upon annealing, the acanthite phase is exhibited. It is proposed that in such a cluster, part of the Ag–SR bond is broken and results in the incorporation of S^{2-} into the lattice and a few thiolate species are protecting the AgSeS core. Based on all of the data presented here (mass, composition, desorption data and diffraction), the cluster has been assigned as $Ag_{56}Se_{13}S_{15}(@SBB_{28}$. This corresponds to a core composition of $Ag_2Se_xS_{1-x}$ composition with SBB protecting ligands.

Cluster composition was further confirmed by the XPS results. Survey spectrum suggested the presence of Ag, Se and S in the purified cluster (Fig. 4A). An expanded region of silver showed Ag $3d_{5/2}$ binding energy at 367.9 eV and Ag $3d_{3/2}$ binding energy at 373.9 eV (Fig. 4B), which indicate the oxidation of Ag ions in the univalent state. The peak at 54.3 eV corresponds to Se 3d and is expanded in Fig. 4C. In the sulfur region, the binding energies of 161.8 eV and 163.0 eV correspond to S $2p_{3/2}$ and S $2p_{1/2}$, respectively.

Utilizing the advantage of the intense red luminescence (QY = 21%) of this cluster, its application was explored towards sensing explored with a view to using it in sensing applications. Ag–S systems have inherent sensitivity towards metal ions.³⁴ Several metal ions such as Cd^{2+} , Cu^{2+} , Hg^{2+} , Pb^{2+} , Ni^{2+} and Zn^{2+} , were used for this experiment, initially in solution phase, which confirmed the selective sensing of Hg^{2+} by this cluster.

Fig. S3A (ESI[†]) shows the reduction of luminescence intensity upon the addition of different metal ions. A relative intensity diagram is plotted in Fig. S3C (ESI⁺). The detection limit of Hg²⁺ ions was found to be 1 ppb (Fig. S3B (ESI⁺)). In order to develop a suitable solid state sensing device, a cluster coated TLC plate was prepared. In general, adsorption on an oxide surface enhances cluster luminescence, because of the reduction in radiative decay channels.^{15,35} A TLC plate was dipped into the cluster solution for 10 min and then dried at room temperature. Fig. 5 shows a photograph of the cluster coated TLC plate under UV light, after the addition of different metal ions. A solid state device also showed drastic quenching of cluster luminescence by Hg²⁺ ions. Concentration dependent luminescence was monitored using the solid state device, and the data are shown in Fig. 6A. Here the change in cluster luminescence as the Hg^{2+} concentration is varied, can be observed. However, the sensitivity was not significant enough for it to be used for visual detection. In order to enhance the visual effect of dye dependent change of cluster luminescence, the TLC plate was pre-coated with a Hg²⁺ insensitive dye, with a different emission wavelength. Fluorescein isothiocyanate (FITC) was used as the dye, which emits a bright green color. The results of such an experiment are shown in Fig. 6B. The combined system shows the emission of the cluster (red). Upon the addition of 500 ppb Hg²⁺ the red emission of the cluster was completely quenched and the underlying FITC emission became prominent. However, on this modified TLC plate, even 1 ppb shows substantial variation in color allowing easy visual detection. This color change is a result of the chemical interaction of Hg²⁺ with the cluster, which is evident from the XPS studies (Fig. S4, ESI⁺). The cluster core interacts with mercuric ions reducing it to the metallic state. The XPS spectrum after



Fig. 4 XPS survey spectrum of the cluster showing the presence of Ag, Se and S (A). Specific regions of Ag 3d, Se 3d and S 2p are shown in (B)–(D).



Fig. 5 Images of a sensing experiment performed using a cluster coated TLC plate. Sensitivity towards different metal ions was tested, at 1 ppm concentration for 2 min of exposure. Mercuric ions are more sensitive.



Fig. 6 Hg²⁺ concentration dependent luminescence quenching is shown in (A). Concentration dependent fluorescence quenching monitored using a FITC dye coated TLC plate (B).

quenching shows mercury in its metallic state (Fig. S4B, ESI[†]). Correspondingly there is also a change in silver binding energy (Fig. S4C, ESI[†]). In order to test the use of this solid state device in real life applications, quenching experiments were done with well water. There was no quenching observed for well water added to a cluster coated TLC plate. Thus, a repeat experiment was done with 1 ppb Hg²⁺ added to well water and quenching was observed. This experiment was also done using a FITC pre-coated TLC plate (Fig. S5, ESI[†]).

Conclusions

In conclusion, a core (AgSeS) shell (thiolate) Ag₂Se cluster system was prepared, which had an enhanced luminescence QY. Using various techniques such as MALDI MS, elemental analysis, TGA and XRD, the 12.5 kDa cluster was assigned to a molecular entity, Ag₅₆Se₁₃S₁₅@SBB₂₈. The QY of the cluster was found to be 21%. This QY is much higher than the reported values for similar cluster systems. It was also shown that the red emission can be used for environmental applications. Incorporation of the cluster into solid supports results in enhanced sensitivity for the sensor and may be useful in developing devices for rapid detection of environmental contaminants.

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