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Introduction

Atomically monodisperse thiolate (-SR) protected noble metal nanoclusters (NCs, also known as nanomolecules^{1,2}) are an

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A scalable synthesis of highly stable and water dispersible $Ag_{44}(SR)_{30}$ nanoclusters[†]

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We report the synthesis of atomically monodisperse thiol-protected silver nanoclusters $[Ag_{44}(SR)_{30}]^m$, (SR = 5mercapto-2-nitrobenzoic acid) in which the product nanocluster is highly stable in contrast to previous preparation methods. The method is one-pot, scalable, and produces nanoclusters that are stable in aqueous solution for at least 9 months at room temperature under ambient conditions, with very little degradation to their unique UV-Vis optical absorption spectrum. The composition, size, and monodispersity were determined by electrospray ionization mass spectrometry and analytical ultracentrifugation. The produced nanoclusters are likely to be in a superatom charge-state of m = 4-, due to the fact that their optical absorption spectrum shares most of the unique features of the intense and broadly absorbing nanoparticles identified as $[Ag_{44}(SR)_{30}]^{4-}$ by Harkness et al. (Nanoscale, 2012, 4, 4269). A protocol to transfer the nanoclusters to organic solvents is also described. Using the disperse nanoclusters in organic media, we fabricated solid-state films of $[Ag_{44}(SR)_{30}]^m$ that retained all the distinct features of the optical absorption spectrum of the nanoclusters in solution. The films were studied by X-ray diffraction and photoelectron spectroscopy in order to investigate their crystallinity, atomic composition and valence band structure. The stability, scalability, and the film fabrication method demonstrated in this work pave the way towards the crystallization of [Ag44(SR)30]^m and its full structural determination by single crystal X-ray diffraction. Moreover, due to their unique and attractive optical properties with multiple optical transitions, we anticipate these clusters to find practical applications in light-harvesting, such as photovoltaics and photocatalysis, which have been hindered so far by the instability of previous generations of the cluster.

> emerging family of model compounds within the technologically important class of thiolate protected metal nanoparticles. Their well-defined structures and discrete size distributions have enabled researchers to envision and engage in profound studies that elucidate their chemical and physical properties:3 size-dependent catalysis,4 quantum-to-plasmon transition,5,6 chirality,7 magnetism,8 and the nature of the thiol-metal interface.9 The central factor permitting such a leap in understanding is the crystallization of NCs into true macroscopically sized crystals and their full structural (metal core and ligand shell) determination by single crystal X-ray diffraction. Typically, stable NCs of high purity are a prerequisite for realizing crystals with the necessary quality for full structural determination. To date, the structures of an impressive number of gold thiolate NCs have been reported.^{1,3} The synthetic methods to produce atomically monodisperse, yet stable, Au NCs reported by several groups remain the key to such progress.³

> In contrast, the full structural characterization of only a few silver thiolate NCs has so far been achieved.^{10,11} Although multiple notable reports on the syntheses of silver thiolate NCs have surfaced,¹²⁻²² most of the products are either polydisperse or unstable, hindering efforts to crystallize them. Of all the

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silver NCs reported so far, $[Ag_{44}(SR)_{30}]^{4-}$ (also known as intense broadly absorbing nanoparticles, IBANs)^{14,23} is of special interest not only as a model compound, but also for its rare and attractive optical properties: multiple strong absorption peaks that cover a broad range of wavelengths (350–950 nm), and an unusually long-lived charge-separated excited state.²⁴ These properties make $[Ag_{44}(SR)_{30}]^{4-}$ a potentially ideal material for light-harvesting in photovoltaics and photocatalysis, should its stability be considerably enhanced. Unfortunately, all previously published reports on $[Ag_{44}(SR)_{30}]^{4-}$ have reported NCs that are easily prone to oxidation at room temperature in a matter of hours.^{14,23,24}

Here we report the synthesis of highly stable and atomically monodisperse $[Ag_{44}(SR)_{30}]^m$ NCs (with a superatom chargestate, *m*, most probably equal to 4–). Moreover, the synthesis is simple and scalable. By using 5-mercapto-2-nitrobenzoic acid as a ligand, we demonstrate that introducing nitro and carboxylic acid functionality in the aryl ligands not only renders the NCs water-soluble, but also stable in solution for a period of at least 9 months. We show that the NCs can be transferred into organic solvents, and use them to fabricate solid films that retain the unique absorption spectrum of $[Ag_{44}(SR)_{30}]^m$. The stability of the NCs facilitated their characterization in solution and in solid-state. Our work enables the practical consideration of $[Ag_{44}(SR)_{30}]^{4-}$ (hereafter referred to simply as $Ag_{44}(SR)_{30}$) in photovoltaics, photocatalysis, and is a milestone towards its crystallization and full structural determination.

Experimental

1 Chemicals

All chemicals including 5,5'-dithiobis (2-nitrobenzoic acid) (DTNBA, 99%), silver nitrate (AgNO₃, 99%), sodium hydroxide (NaOH), sodium borohydride (NaBH₄, 99.99% metals basis), and tetramethylammonium hydroxide (TMAH, 23%) were purchased from Sigma Aldrich and used without further purification.

2 Characterization techniques

Nuclear magnetic resonance (NMR) spectra were recorded at 298 K on a Bruker 600 AVANAC III spectrometer equipped with a Bruker BBO multinuclear probe.

Mass spectra were collected using a Waters SynaptTM G1 Q-Tof High Definition Mass Spectrometer. The NC sample was dispersed in methanol (HPLC grade) and the solution was electrosprayed in negative mode by using a stainless steel syringe. The instrument parameters were maintained as follows: mass range 400 to 4000 Da; capillary voltage -2.1 kV; detector voltage 1.7 kV; extraction cone voltage 2.1 V; sampling cone voltage 10.0 V; source temperature 90 °C; desolvation temperature 200 °C; optics mode V. All the mass spectral data were processed using Masslynx 4.1 software (Waters Corp.).

Sedimentation velocity-analytical ultracentrifugation (SV-AUC) experiments were performed using an Optima XL-A analytical ultracentrifuge from Beckman Coulter with an absorbance optical detection system and an An-60 Ti rotor. The sedimentation and diffusion coefficient (*s* and *D*) distributions

were calculated using Ultrascan III (version 1.0, revision 1349),²⁵ utilizing a procedure similar to the previous work.²³ After calculating *s* and *D*, the molecular weight was determined based on the work of Carney *et al.*²⁶

Transmission electron microscopy (TEM) images were obtained using a TitanG2 80-300 instrument, equipped with an image-corrector from CEOS. An energy-filter from Gatan Inc. was used at an acceleration voltage of 300 kV and an energy-slit of width 10 eV to reduce the amount of inelastically scattered electrons for improving the image contrast in high resolution (HR) TEM micrographs of these NCs.

Large angle powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance with a Cu source. A dispersion of $Ag_{44}(SR)_{30}$ NCs in methanol was drop-cast on a silicon single crystal substrate to avoid any signal contribution from the background.

X-ray photoelectron spectroscopy (XPS) measurements were done on a UHV Omicron surface analysis system, equipped with a SPHERA U7 hemispherical energy analyser with a 7-channel MCD detector, high intensity monochromated Al K α X-rays and He I radiation sources, and an XM 1000 monochromator.

The ultraviolet photoemission spectroscopy (UPS) study was carried out at the Canadian Light Source. The photon energy used for this study was 36 eV with a total energy resolution of 30 meV. All spectra were collected by a Scienta SES100 spectrometer at normal emission and room temperature.

The UV-Vis absorption spectra of silver NCs in solution were recorded using a JAZZ spectrophotometer (Ocean Optics).

3 Synthesis and purification of Ag₄₄(SC₆H₄O₄N)₃₀ NCs

In a 25 mL Erlenmeyer flask, DTNBA (9.91 mg, 25 mmol) was stirred in NaOH aqueous solution (20 mL, 1 M). The orangish solution turned to dark yellow indicating the cleavage of the disulfide bond yielding 5-mercapto-2-nitrobenzoic acid (MNBA). An aqueous solution of AgNO₃ (8.5 mg, 50 mmol, 5 mL) was then added to the MNBA solution. The colour turned greenish yellow indicating the formation of an Ag–S complex. A fresh aqueous solution of NaBH₄ (1 mg, 2 mL) was then used to reduce the complex. The solution turned dark brown immediately and gradually changed to dark red under vigorous stirring for 4 h, indicating the formation of $Ag_{44}(SR)_{30}$ NCs. The clusters were purified by repeated precipitation with 50% methanol followed by repeated centrifugation at 9000 rpm for 10 min and decantation of the supernatant until it became colourless.

4 Film fabrication

Films of clusters were drop-cast from methanol. In order to disperse the NCs in methanol, the purified NCs in water were precipitated one more time with methanol, and then mixed with 500 μ L of TMAH. The solvent (water to methanol) exchange was established by concentrating the particle solution to 10% of its original volume in centrifuge filters (10 kDa M_w cut-off) and reconstituting the rest of the volume with pure methanol. This cycle was repeated 3–4 times to obtain a stable solution of the clusters in methanol with trace amounts of water.

Results and discussion

1 Synthesis

Recently, thiolated $[Ag_{44}(SR)_{30}]^{4-}$ NCs protected by 4-fluorothiophenol, 3-fluorothiophenol, 2-fluorothiophenol, 4-mercaptobenzoic acid, (2-mercapto-5-methylphenyl)methanol, and 4-methylbenzene-1,2-dithiol have been reported.¹⁴ These clusters exhibited unique absorption in the visible and near-IR regions of the optical spectrum.^{14,23} The exact molecular formula and the monodispersity of these NCs were determined by ESI-MS and SV-AUC.²³ Major shortcomings of the reported synthesis protocol of these NCs were their instability (*i.e.* growth into larger particles in a few hours at room temperature), easier oxidation, cumbersome purification, and being only stable if refrigerated at -4 °C.

Herein, we report the synthesis of Ag₄₄(SR)₃₀ NCs (with most probably a superatom charge of 4-, *vide infra*) that are stable for at least 9 months at room temperature and under ambient conditions in aqueous media. This facilitates their characterization and paves the way for their use in practical applications. In this work, we used 5-mercapto-2-nitobenzoic acid (MNBA) as a ligand for Ag₄₄(SR)₃₀ NCs. By using stabilizing ligands with nitro and carboxylate electron withdrawing groups, we obtained highly stable NCs with the same optical properties and molecular assignment as previously reported $Ag_{44}(SR)_{30}$, yet stable for several months at room temperature and under ambient conditions. The structure of the ligand and the reaction scheme are depicted in Scheme 1. Briefly, the cleavage of the disulfide bond of 5,5'-dithiobis (2-nitrobenzoic acid (DTNBA)) was achieved by vigorous stirring in 1 M aqueous NaOH solution for around 1 h to form MNBA. Subsequently, an equimolar solution of Ag salt in water was added and the reaction mixture was stirred at room temperature for another hour to ensure the formation of an Ag-S complex. Finally, NaBH₄ was added and the solution was left overnight under vigorous stirring. The resulting crude nanoclusters showed at least five distinct absorption peaks in the UV-visible-NIR region with absorption maxima at 400, 480, 550, 650, and 850 nm (see the black curve in Fig. S1[†]). These absorption peaks became even sharper and more pronounced after the purification step (see the red curve in Fig. S1[†]). A typical reaction yielded approximately 4.3 mg (50% conversion of Ag from AgNO₃) of NCs. However, the reaction can be scaled up by at least a factor of 40 (see Fig. S2⁺).

2 Stability

In contrast to the previous reports on $Ag_{44}(SR)_{30}$ that were stable for only a few hours, the MNBA-stabilized NCs reported in this



Scheme 1 Synthesis of Ag₄₄(SR)₃₀ nanoclusters.

work were colloidally and chemically stable for at least 9 months under ambient conditions as shown in Fig. 1a. The choice of MNBA as a ligand was guided by our previous observation that the stability of the formed clusters was dependent on the functional groups on the phenyl ring of the aryl ligands.¹⁴ In particular, 4-mercaptobenzoic acid (4-MBA)-stabilized NCs were more stable than the 4-fluorothiophenol (4-FTP) NCs.¹⁴ This suggested that the stability of these clusters might be due to the electron withdrawing groups (EWGs) of the ligand. In order to test this hypothesis, we investigated the use of 3-mercaptobenzoic acid (3-MBA) as a ligand, while the stability of the formed clusters was monitored by UV-Vis absorption spectroscopy (see Fig. S3†). These studies indicated that the resulting clusters were stable for 3 to 4 days under ambient conditions at basic pH.

We experimented with various derivatives of MBA and found that MNBA (Scheme 1, step 2), which contained a nitro group at the *para* position of the phenyl ring with respect to



Fig. 1 UV-Vis spectra of (a) Ag_{44} (MNBA)₃₀ NCs in 1 M NaOH aqueous solution 24 hours (black), 9 months (red) after synthesis; and (b) NCs transferred into methanol (black) and in a solid form (red).

thiol and adjacent to the carboxylic acid group, provided the best stability, likely due to the combined effect of two EWGs. Additionally, both groups are relatively hydrophilic, and thereby enhanced the colloidal stability of the resulting NCs in aqueous media. It is worth noting that when 4-nitrobenzoic acid was used as a ligand, the resulting clusters were highly unstable with aggregation quickly occurring after synthesis, suggesting that the electron withdrawing capabilities of the nitro group is not enough to endow the NCs with the desired stability.

We were also able to transfer the NCs to methanol using TMAH (*vide supra*) as a positively charged counterion to the cluster, which is overall negatively charged,^{14,23} and used the resulting solution to fabricate solid films. The use of volatile organic solvents aids in the fabrication of smooth films using solution based methods such as drop-casting or spin-coating. The NCs in both methanol solution and solid-state retained the overall unique absorption spectrum of the original synthesized clusters (see Fig. 1b).

To the best of our knowledge, this is one of the first reports on $Ag_{44}(SR)_{30}$ NCs (*vide infra*) that are stable, scalable and can be easily purified. The stability of the cleaned clusters facilitated their further characterization in liquid solution and in solid-state.

3 Size and composition

The size, composition, and chemical structure of the resulting Ag NCs were investigated using a combination of different analytical techniques including ESI, AUC, HRTEM, Powder XRD, XPS, and ¹H NMR. The results from these studies are discussed below.

ESI-MS has become a potent technique used in measuring the molecular weight of noble metal thiolate NCs.^{23,27} The full spectrum of the resulting $Ag_{44}(SR)_{30}$ NCs, measured in negative mode, is shown in Fig. 2 together with the theoretical spectrum for $Ag_{44}(SR)_{30}$. As apparent from Fig. 2, the four major peaks corresponding to 4, 5, 6 and 7 charge states of the resulting NCs are in a good agreement with their corresponding theoretical values. The inset of Fig. 2 shows the expansion of the 5-charge state centered at m/z 2165 Da, from which the molecular weight of the resulting NCs was calculated to be *ca.* 10.8 kDa. A common problem in mass spectrometric characterization of metal nanoclusters is that they often undergo fragmentation during the process of ionization. We can exclude this possibility because the MS results are in close agreement with those of analytical ultracentrifugation (*vide infra*).

SV-AUC is a complementary characterization technique to TEM and mass spectrometry and is used to determine the homogeneity and approximate size of macromolecules and nanoparticles in solution. In previous reports we successfully used SV-AUC to determine the approximate molecular weight, density, and size distribution of Au and Ag NCs, by measuring their sedimentation (s) and diffusion (D) coefficient distributions in solution.

The *s* and *D* distributions of the synthesized $Ag_{44}(SR)_{30}$ NCs in 1 M NaOH aq. are shown in Fig. 3. The distributions show that the clusters are homogeneous; at least 94% of the sample is



Fig. 2 Negative ion ESI-MS of $Ag_{44}(MNBA)_{30}$ NCs in comparison with the theoretical spectrum of $Ag_{44}(MNBA)_{30}$. The inset shows the expansion of the 5-charge species.



Fig. 3 2D plot of sedimentation coefficients (s) and diffusivities (D) of the NCs.

comprised of one species with $s = 3.57 \times 10^{-13}$ s. The diffusion coefficient (*D*) corresponding to this species is 1.24×10^{-6} cm² s⁻¹. The remaining species at around $s = 3.3 \times 10^{-13}$ s are likely the same species that did not sediment ideally due to particle-particle interaction in solution. For the most abundant species, we found that the molecular weight is *ca.* 11.1 kDa. SV-AUC data on the clusters in solution are atomically monodisperse and corroborate the mass spec assignments of Ag₄₄(SR)₃₀.

HR-TEM was used to provide the insights into the core size and morphology of the $Ag_{44}(SR)_{30}$ NCs. In general, TEM cannot be used to determine the exact structure of clusters in this size range³ and is also prone to imaging and sample preparation artefacts because (i) the electron beam may alter the clusters; (ii) the low-contrast of the smallest clusters results in a bias in



Fig. 4 (a) TEM image of the synthesized NCs. (b) A magnified HR-TEM image of a single cluster.

the size statistics and (iii) different orientations of the same cluster are hard to distinguish from the heterogeneous distribution of clusters. Nevertheless, from TEM images, one can see that the particle shapes are not spherical (Fig. 4a) and that they have crystalline Ag cores (Fig. 4b), with a diameter size in the range of *ca.* 1.5–2.5 nm.

Powder XRD. For more accurate core size determination of the cluster, we performed large-angle powder XRD (see Fig. 5). The broad peak shown in Fig. 5 overlaps with the (111) and (200) reflections of bulk fcc-Ag. Thus we fit two Gaussian peaks around these positions and used Scherrer's equation to estimate the crystal size.²⁸ We found that the core size is 1.39 nm, which is in good agreement with the core sizes inferred from ESI-MS and SV.

The XPS survey spectrum of $Ag_{44}(SR)_{30}$ NCs drop-cast on the glass/ITO substrate is shown in Fig. 6. The spectrum reveals the presence of Ag, S, C, N, O, and a residual amount of Na; no other elements were detected. The Ag 3d5/2 peak is at 366.9 eV. This value is 1.1 eV lower in binding energy (BE) compared to the reported value for bulk Ag (368 eV). As for sulfur, the S 2p peak is observed at 161.3 eV. This value does not correspond either to free thiols or to disulfides, whose expected BEs are higher than



Fig. 5 Powder X-ray diffraction of the (111) and (200) reflections of $Ag_{44}(MNBA)_{30}$ NCs (black) plotted *versus* $s = 2 \sin \theta / \lambda \ln 1 \text{ nm}^{-1}$. The bars (at the bottom) correspond to the reflections of bulk fcc-Ag. The greenish curves correspond to the Gaussian fitting of the spectrum to calculate the FWHM of the two peaks while the red curve is the cumulative peak fit.



Fig. 6 XPS survey of Ag₄₄(MNBA)₃₀ NCs.

163 eV; it is close to the reported value of metal sulphides (161.1–162.2 eV). 29

High-resolution XPS measurements were performed in order to quantitatively analyse the elemental composition of the $Ag_{44}(SR)_{30}$ NCs. The integration of the area under Ag 3d and S 2p peaks gave 43.3% Ag and 56.7% S atomic concentration, and in reasonably good match with the values calculated for $Ag_{44}(SR)_{30}$, where there are 40.5% Ag and 59.5% S.

¹H NMR. High-resolution ¹H NMR was used to investigate the ligand–shell structure of the nanoclusters. NMR spectroscopy has previously shown great promise as a tool to understand the chemical environments and the morphology at the metal–ligand interface.^{30–32} Fig. 7 shows the aromatic region of the ¹H NMR spectra of the ligand and of a dispersion of Ag₄₄(SR)₃₀ NCs.



Fig. 7 Aromatic region of ¹H NMR spectra of (a) free starting material ligands; the inset shows the chemical structure of DTNBA and (b) Ag_{44} (MNBA)₃₀ NCs dispersed in 1 M NaOH in D₂O; integration of the cluster's protons are displayed below their respective peaks.

By inspection of the NMR spectra of the starting material (5,5'dithiobis (2-nitribenzoic acid)) and the formed Ag₄₄(MNBA)₃₀ NCs, it is clear that all the peaks of the ligands attached to the NCs are shifted upfield. Such a shift is usually related to the different surrounding environment of the ligands. The NMR spectrum of the resulting NCs showed the presence of two different ligand environments with the ratio of 3 : 1 (see integration of proton peaks in Fig. 7b). One proton set has a singlet at 7.65 and doublets at 7.18 and 7.2, while the other one has a singlet at 7.45 and two doublets at 6.3 and 6.6. The observed upfield shifts are indicative of the shielding effect of the clusters on the ligand protons.³³ The full ¹H NMR spectrum of the NCs along with the chemical shift assignments is shown in Fig. S4.†

4 Optical and electronic characteristics

The UV-Vis absorption spectrum of the NCs shows at least five distinct absorption peaks at ~400, ~480, ~550, ~650 and \sim 850 nm, similar to the reported spectrum of the [Ag₄₄(4- FTP_{30}^{4-} NCs,^{14,23} (see Fig. 8). Multiple absorption peaks in the visible-NIR region are indicative of the molecular-like electronic structure. It is well known that the optical absorption transitions of discrete noble metal NCs in this size range, which behave like superatom complexes,³⁴ are sensitive to the overall charge of the cluster.35 Indeed, one can expect the visible and NIR optical transitions of an $[Ag_{44}(SR)_{30}]^{4-}$ cluster to be even more sensitive to perturbation to its charge-state because they correspond to charge-separated excited states.24 Thus the similarity between the optical absorption spectra of the previously reported $[Ag_{44}(SR)_{30}]^{4-}$ and the clusters in this work suggests that the two are identical in the superatom chargestate, in addition to the stoichiometric formula and size, which were confirmed by ESI mass spectrometry and other techniques (vide supra).

The valence band structure of the NCs deposited onto an Au film is shown in Fig. 9. The (dashed) black curve corresponds to



Fig. 8 UV-Vis spectra of Ag_{44} (MNBA)₃₀ NCs (red curve) in comparison with Ag_{44} (4-FTP)₃₀ ones (black curve). The inset shows the chemical structures of MNBA and 4-FTP.



Fig. 9 Normal emission UPS spectra of Ag_{44} (MNBA)₃₀ NCs (red curve) in comparison with the Ag single crystal (black curve). The inset shows a zoomed-in around B.E. = 0.

the spectrum of the Ag single crystal and consists of the seven features at 2.8, 3.9, 5.3, 6, 7.5, 10.3 and 11.7 eV. The spectrum of the NCs (up to some extent) resembles the valence band structure of the bulk Ag that was measured on the Ag (111) single crystal and denoted as "Ag single crystal". The valence band structure of the bulk Ag shows the Ag d-band with the d-band centered around 5.1 eV and the sharp Fermi edge (inset in Fig. 9), consistent with previous reports.³⁶

What differentiates the electronic structure of the $Ag_{44}(MNBA)_{30}$ NCs from the bulk Ag is the absence of the intensity at the Fermi edge region; the onset of the NCs spectrum is around 0.9 eV away from the Fermi edge (the inset in Fig. 9), which is strong evidence of the semiconducting nature of the $Ag_{44}(MNBA)_{30}$ NC films. The other clearly noticeable difference is the feature at 9.7 eV observed in the NC's spectra that is not present in the spectra of bulk Ag. This feature is tentatively attributed to the organic content of the film, although the nature of the valence band structure *e.g.* the origin of the spectral features is not well understood at the moment and is the subject of further investigation.

Conclusion

A simple, scalable and reproducible protocol for the synthesis of highly stable, water-soluble and atomically monodisperse $Ag_{44}(SR)_{30}$ NCs is described. The clusters can be stored at room temperature for many months, and can be used to fabricate films that retain the unique optical absorption properties of the dispersed NCs. We anticipate that this development will facilitate further studies of the cluster's physical and electronic properties, and crystallization for full structural determination through single crystal X-ray diffraction. Moreover, the favourable optical properties of $Ag_{44}(SR)_{30}$ combined with stability puts the utilization of the clusters in light harvesting applications within reach. Those topics are the subject of our current and future investigation.

Conflict of interest

The authors declare no competing financial interests.

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