# Nanoscale

## PAPER

Cite this: Nanoscale, 2014, 6, 8024

# Emergence of metallicity in silver clusters in the 150 atom regime: a study of differently sized silver clusters†

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We report the systematic appearance of a plasmon-like optical absorption feature in silver clusters protected with 2-phenylethanethiol (PET), 4-flurothiophenol (4-FTP) and (4-(t-butyl)benzenethiol (BBS) as a function of cluster size. A wide range of clusters, namely, Ag<sub>44</sub>(4-FTP)<sub>30</sub>, Ag<sub>55</sub>(PET)<sub>31</sub>, ~Ag<sub>75</sub>(PET)<sub>40</sub>,  $\sim Ag_{114}(\text{PET})_{46}, \ Ag_{152}(\text{PET})_{60}, \ \sim Ag_{202}(\text{BBS})_{70}, \ \sim Ag_{423}(\text{PET})_{105}, \ \text{and} \ \sim Ag_{530}(\text{PET})_{100} \ \text{were prepared. The UV}/$ Vis spectra show multiple features up to  $\sim Ag_{114}$ ; and thereafter, from  $Ag_{152}$  onwards, the plasmonic feature corresponding to a single peak at ~460 nm evolves, which points to the emergence of metallicity in clusters composed of ~150 metal atoms. A minor blue shift in the plasmonic peak was observed as cluster sizes increased and merged with the spectrum of plasmonic nanoparticles of 4.8 nm diameter protected with PET. Clusters with different ligands, such as 4-FTP and BBS, also show this behavior, which suggests that the 'emergence of metallicity' is independent of the functionality of the thiol ligand.

Received 6th February 2014 Accepted 9th May 2014

DOI: 10.1039/c4nr00679h

www.rsc.org/nanoscale

### Introduction

The strong collective oscillation of electrons referred to as plasmon resonance,1 which produces characteristic colors in optical absorption, is the most fascinating property of noble metal nanoparticles,<sup>2-5</sup> and is the basis for most of their applications.<sup>6-8</sup> The occurrence of this collective phenomenon is attributed to the existence of metallicity9 in such systems; therefore, it is important in the cluster size regime of metals. Investigation of electronic structures by photoelectron spectroscopy has suggested the emergence of metallicity in the 200-400 atom window in several naked (ligand-free) metal systems such as Hg, Cu and Au.<sup>10-12</sup> For several metals such as Na, K, and Al, the appearance of plasmon has been extensively studied.<sup>13-17</sup> Investigations of single particle conductivity by scanning electron spectroscopy and similar studies18 have also proposed the emergence of metallicity in this size window. On the other hand, large nanoparticles protected by monolayers of organic molecules, possessing metallicity in transport measurements<sup>19</sup> have been brought into the cluster size regime by core etching protocols<sup>20-22</sup> wherein distinct luminescence in the visible

region, characteristic of clusters has been observed.23 Therefore, metallicity occurs beyond the regime of these clusters<sup>24-31</sup> but below the size regime of nanoparticles in the range of silver nanoclusters. Thiolated gold clusters are normally more stable as compared with silver clusters because Ag(0) is easily oxidisable under atmospheric conditions. Several gold clusters, such as Au25,32,33 Au28,34 Au36,35 Au38,36 and Au102,37 have been crystallized recently, and there are many reports of their mass spectrometric assignments.<sup>38,39</sup> Recently, Dass et al.<sup>40</sup> and Jin et al.<sup>41</sup> demonstrated the plasmonic feature in gold for ~76 kDa particles protected by monolayers. In the case of silver, although clusters analogous to gold have not been prepared, there are reports of  $Ag_{7,8}$ ,<sup>22</sup>  $Ag_9$ ,<sup>30</sup>  $Ag_{32}$ ,<sup>27</sup> and  $Ag_{152}$ <sup>42</sup> and a few others such as Ag14,43 Ag1644 and Ag44;26,31 the latter clusters have been crystallised.

In this paper, we report the emergence of plasmon-like optical absorption spectra in thiol-protected silver clusters in solution, which points to the appearance of metallicity in clusters composed of ~150 metal atoms. Our proposal of emergence of plasmon resonance is in accordance with the studies reported so far12 and points to similar results in other metal systems.6-8

### Experimental section

#### Materials

All the chemicals were commercially available and were used without further purification. Silver nitrate (AgNO<sub>3</sub>, 99% Aldrich), silver trifluroacetate (AgCOOCF<sub>3</sub>, 99%, Aldrich),



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<sup>†</sup> Electronic supplementary information (ESI) available: Details of laser dependent fragmentation, SEM-EDAX of  ${\sim}Ag_{202},$  TEM of  ${\sim}Ag_{530}$  and nanoparticles and corresponding energy-dependent UV/Vis spectra, DLS, and comparative MALDI MS. See DOI: 10.1039/c4nr00679h

sodium borohydride (NaBH<sub>4</sub>, 99.9%, Aldrich), tetraoctylammonium bromide (TOAB, 99%), 2-phenylethanethiol (PET, 98%, Aldrich); 4-(*t*-butyl)benzenethiol (BBS, 98%, Aldrich), 4flurothio phenol (4-FTP, 98%, Aldrich) ethanol (Changshu Yangyuan Chemical, China, AR grade), acetonitrile, tetrahydrofuran, methanol and toluene (all obtained from Ranken, AR grade) were used in this work.

#### Synthesis of PET-protected clusters

The clusters protected with PET were prepared using the solid state method,<sup>22</sup> and a solution-phase synthetic route was followed for BBS-protected clusters. The clusters were synthesized by carefully controlling the conditions and were purified using solvent extraction protocols. These can be clearly understood in the light of Table 1 given below, which lists the synthetic details. Initially, at room temperature (35-40 °C in Chennai, relative humidity, 31%) X mg of AgNO<sub>3</sub> and Y µL of PETH were ground thoroughly in a clean agate mortar using a pestle. In some cases, tetraoctylammonium bromide (TOAB) was also used along with the ligand (see Table 1). The color of the mixture changed to pale orange, showing the formation of silver thiolate. To this mixture, Z mg of solid NaBH<sub>4</sub> was added and the contents were mixed well. 5 mL of ethanol was added for washing the mixture. The mixture was maintained for 15-30 s until the color changed from pale orange to deep grey, which happened within 1 min. The contents were then taken in a centrifuge tube and centrifuged at 1600 rpm. The centrifugate was removed (except in the case of Ag<sub>55</sub>, where ethanol was used as the extracting solvent) and the residue was dissolved in *Q* mL solvent (S). The clusters obtained from the solvent extract were dark brown in color. The synthesis of ~Ag<sub>530</sub> required more time; initially, ~Ag<sub>75</sub> clusters were formed but after one day they transformed to  $\sim Ag_{530}$ , which is stable. TOAB facilitated this transformation.45

#### Synthesis of the BBS-protected cluster

20 mg of AgNO<sub>3</sub> was dissolved in 3 mL of methanol, and 3 mL of toluene was also added to this solution. Then BBS (1 : 6 mole ratios with respect to silver) was added under stirring, and an Ag-thiolate complex was formed. During this process, the color of the solution changed from deep yellow to light yellow. After 30 min, 2 mL fresh ice-cold solution of NaBH<sub>4</sub> (1 : 10 mole ratio

**Table 1** Amounts of starting materials used for synthesizing various clusters<sup>a</sup>

with respect to silver) was added. The yellow color changed to dark brown. Stirring was continued for 30 min. Two separate layers were observed; the top layer contained the cluster, which was removed and further characterized.

#### Synthesis of Ag<sub>44</sub> cluster

The Ag<sub>44</sub> cluster was synthesised using a reported procedure.<sup>28</sup>

#### Instrumentation

UV/Vis spectra were measured with a Perkin Elmer Lambda 25 instrument in the range of 200-1100 nm. The spectra were corrected by the Jacobian factor (see below). High resolution transmission electron microscopy of clusters was carried out with a JEOL 3010 instrument with a UHR polepiece. The samples were drop-cast on carbon-coated copper grids and allowed to dry under ambient conditions. Matrix-assisted desorption ionization mass spectrometry (MALDI MS) studies were conducted using a Voyager-DE PRO Bio-spectrometry Workstation (Applied Bio-systems). A pulsed nitrogen laser of 337 nm was used for the MALDI MS studies. Mass spectra were collected in the positive ion mode and were averaged over 200 shots. For sample preparation, the as-synthesized clusters were mixed with DCTB (trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile) matrix (12.5 mg mL<sup>-1</sup> in toluene) in 1:1 and 2:1 volume ratios, followed by an immediate spotting on the MALDI plate. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) measurements were performed with a FEI QUANTA-200 SEM. For measurements, samples were drop-cast on an indium tin oxide (ITO)-coated glass as well as on carbon tape and subsequently dried under vacuum. DLS was performed with a Horiba instrument. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Omicron ESCA probe spectrometer with polychromatic MgKa Xrays ( $h\nu = 1253.6$  eV). The samples were spotted as drop-cast films on a sample stub. A constant analyzer energy of 20 eV was used for the measurements.

### **Results and discussion**

The core size of each cluster sample was characterized by matrix assisted laser desorption ionization mass spectrometry (MALDI

Clusters	AgNO <sub>3</sub> (X/mg)	TOAB (in mg)	PETH $(Y/\mu L)$	NaBH <sub>4</sub> (Z/mg)	Solvent (Q/mL)	Yield (%)	Stability <sup><math>\Phi</math></sup> (day)
Ag <sub>55</sub>	23	5	100	25	Ethanol (5)	64%	3
$\sim Ag_{75}$	20	—	Glutathione* (12.5 mg)	Formic acid* (200 μL)	Water*	—	8
$\sim Ag_{114}$	23	—	100	25	$CH_3CN(5)$	72%	4
Ag <sub>152</sub>	23	—	100	25	Toluene (5)	82%	$10^{\$}$
$\sim Ag_{423}$	23	—	100	25	50 : 50 mixture of toluene–methanol (5)	64%	5
$\sim Ag_{530}$	47	34	200	30	Toluene (20)	76%	$14^{\#}$
Ag NP	47	_	100	30	Toluene (5)	84%	30

 $a^{a}$  \*, # and \$ refer to the corresponding references given below and  $\Phi$  refers to stability in the ambient laboratory conditions. \* ref. 46, \$ ref. 42, # ref. 45.

MS) with DCTB as the matrix (Fig. 1), which is effective for organic soluble clusters.<sup>42,46-48</sup> The spectra show the existence of eight distinctly different clusters with characteristic peaks at 10.3, 13.7, 18.6, 24.5, 33.4, 60 and 70.9k. Assuming the ions to be monocationic, as suggested by their peak width, the clusters responsible for these peaks were assigned to  $Ag_{55}(PET)_{31}$ ,  $\sim Ag_{75}(PET)_{40}$ ,  $^{46} \sim Ag_{114}(PET)_{46}$ ,  $Ag_{152}(PET)_{60}$ ,  $^{42} \sim Ag_{202}(BBS)_{70}$ ,  $\sim Ag_{423}(PET)_{105}$ , and  $\sim Ag_{530}(PET)_{100}$ ,<sup>45</sup> respectively, (where peaks were ill defined in a few cases, the composition is indicated with a ' $\sim$ ' symbol, as practiced by other researchers<sup>49</sup>). Compositions suggested here have also been supported by elemental analysis and XPS (see below). In most of the cases (labeled as 'a', 'b', 'c', 'd' in Fig. 1), the spectra correspond to sharp and single features. This is especially noticeable in 'a' and 'd' corresponding to Ag<sub>55</sub> and Ag<sub>152</sub>, respectively. For 'b', there is a weak feature at the high mass side and for 'c', there is a weak shoulder at the high mass side. For these reasons, we suggest only approximate compositions for these cases. Detailed characterization of each cluster is beyond the scope of this work, and some of the clusters (Ag<sub>44</sub>, ~Ag<sub>75</sub>, Ag<sub>152</sub> and ~Ag<sub>530</sub>) have been described previously.<sup>26,28,31,42,45,46</sup> It is important to note that the spectra were collected at the threshold laser powers (fluences) where observable fragmentation is not observed. Above a characteristic laser power, fragmentation was observed, normally resulting from the loss of the monolayer, AgSR, Ag(SR)<sub>2</sub> or R.42,46 Such systematic losses and fragmentation arising from

cleavages in  $Ag_n$ -S-R are well-known on UV laser irradiation, and such processes have been useful in understanding the core sizes.<sup>50</sup> For example, in the case of  $Ag_{152}$ PET<sub>60</sub>, we could see a gradual fragmentation with an increase in laser power (Fig. S1, ESI†) and above a certain laser power, no further fragmentation was observed. The spectra are also composed of a few other clusters of higher masses (traces 'e', 'f' and 'g'), which exhibit multiple features. Specific clusters have not been obtained in such cases to date.

However, even in those cases the spectra are dominated by one major feature with a few other clusters existing with reduced intensity. Another interesting feature was the full width at half maximum (FWHM) of each spectrum. The FWHM varied from 1.5 to 5k. In a, c, d and f, the peak width is very small (below 3k), which is not observed in any silver clusters reported to date.

It is important to note that all the peaks are broad in comparison with molecules of similar mass such as smaller proteins. However, we must note that the peak is sharper than protein-protected silver, gold and silver–gold alloy clusters, which are similar to those considered here.<sup>51–53</sup> In Fig. S2A, ESI,† we have plotted the MALDI MS spectra of the Ag<sub>152</sub> cluster (of the most narrow width), a small protein, a lysozyme in its native state and that of a lysozyme–gold cluster (all in linear positive ion mode). We see that while the native protein spectrum is sharper ( $\Delta m = 0.3$  Da), the mass feature of the protein cluster is



Fig. 1 MALDI MS spectra (collected in positive mode) of silver clusters prepared in solution. All the clusters were purified by solvent extraction before spotting for MALDI MS studies. Threshold laser fluence was used throughout the experiment to avoid fragmentation. The spectra show a series of clusters with peak maxima ranging from 10.2 to 70.9k. Almost all the spectra (except 'f' and 'g', which have some other features with reduced intensity) show sharp single features, confirming the formation of one dominant cluster in each case. The FWHM varied from 1.5 to 5 kDa. The peaks (from bottom to top) were assigned as:  $Ag_{55}(PET)_{31}$  [a],  $\sim Ag_{75}(PET)_{40}$  [b],  $\sim Ag_{114}(PET)_{46}$  [c],  $Ag_{152}(PET)_{60}$  [d],  $\sim Ag_{202}(BBS)_{70}$  [e],  $\sim Ag_{423}(PET)_{105}$  [f], and  $\sim Ag_{530}(PET)_{100}$  [g]. Spectra have been shifted vertically for clarity.

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broader ( $\Delta m = 2.5$  Da) and the width is comparable to that of the silver cluster. This broadening of the protein–gold cluster is due to the changes in the native structure of the protein upon cluster formation. It may also be noted that the protein-protected clusters shown are those of Au, which has only one isotope. In the case of silver, there is a natural isotope width, and its spread is large in the case of a multi-atom cluster (see below). The data suggest that the inherent width in silver clusters is comparable to that of molecular systems of similar masses. For comparison, the MALDI MS of Ag<sub>152</sub> cluster was plotted along with the well-characterised Ag<sub>44</sub> cluster (Fig. S3, ESI†). The data suggest that the spectra of silver clusters are broad in nature even if they are atomically precise.

Electrospray ionization (ESI) is a preferred method for retrieving data on several thiolated clusters. However, for silver clusters, ESI MS is still not ideal because intact ionization is difficult. More ESI MS data are available for gold clusters; however, it is important to note that gold has only one isotope, whereas silver has two isotopes at m/z 107 and m/z 109 with 50: 50 intensity. This adds additional width to the mass feature of silver clusters. In addition, silver-sulfur binding is weaker, which makes the intact cluster less stable, and the ligand losses occur upon ionization. Both these factors contribute to the increased width of the mass spectrum of silver clusters (in comparison with that of gold). In the case of  $Au_{25}PET_{18}$ , the spectrum (Fig. S2B, ESI<sup>+</sup>) is measurable with improved resolution in the reflectron mode. Because typical reflectron measurements are limited to m/z 10 000, the present silver clusters at  $m/z > 10\ 000$  could not yield better peak shapes in such measurements.

The SEM/EDAX data further support the composition of the clusters. Fig. 2 shows the corresponding EDAX spectra of Ag<sub>55</sub>

(a),  $\sim Ag_{75}$  (b),  $\sim Ag_{114}$  (c),  $Ag_{152}$  (d),  $\sim Ag_{423}$  (e) and  $\sim Ag_{530}$  (f). Here, clusters were drop-cast on indium tin oxide (ITO)-coated glass plates. The spectrum of  $\sim Ag_{202}$  was collected from a dropcast sample (on a carbon tape) and is shown in Fig. S4, ESI.† The expected elements are seen in each case, and the Ag : S ratios were 1:0.60, 1:0.58, 1:0.39, 1:0.43, 1:0.40, 1:0.34 and 1:0.37 for Ag<sub>55</sub>,  $\sim Ag_{75}$ ,  $\sim Ag_{114}$ , Ag<sub>152</sub>,  $\sim Ag_{202}$ ,  $\sim Ag_{423}$  and  $\sim Ag_{530}$ , respectively, whereas the expected ratios are 1:0.56, 1:0.53, 1:0.36, 1:0.39, 1:0.34, 1:0.25 and 1:0.18. For the last two cases, there is an excess amount of thiol in the sample, which is probably required for cluster stabilisation.<sup>42</sup> As  $\sim Ag_{423}$ and  $\sim Ag_{530}$  samples are not pure, as seen from their mass spectra, their atomic ratios deviate significantly from the expected ratios.

These clusters with precise core sizes are observable in TEM, where well-defined cores ranging from 1.12 nm to 4.0 nm are observed (Fig. 3 and S5, ESI<sup>†</sup>). The particle size increases with the nuclearity of the cluster. The size distribution shown in the insets of each of these images (Fig. 3) confirmed that the synthetic protocol yielded the desired results. A narrow size distribution suggests the monodispersity of the as-synthesised clusters. The average core diameters were 1.12, 1.32, 1.75, 2.0, 2.61 and 3.20 nm for Ag55, ~Ag75, ~Ag114, Ag152, ~Ag202 and ~Ag<sub>423</sub>, respectively. Polydispersity is seen in image 'f', which in agreement with the mass spectrum (Fig. 1f). The cluster  $\sim Ag_{530}$ is about 3.61 nm in diameter (Fig. S5, ESI<sup>+</sup>), which also exhibits polydispersity. To further support monodispersity, dynamic light scattering measurements were carried out for the PETprotected clusters (Fig. S6, ESI<sup>†</sup>), which also shows a narrow size distribution for smaller clusters up to  $Ag_{152}$ . For  $\sim Ag_{423}$ , the peak becomes broader, as expected from MALDI MS data, which suggests the existence of other species in minor proportions.



Fig. 2 SEM/EDAX of Ag<sub>55</sub> (a), ~Ag<sub>75</sub> (b), ~Ag<sub>114</sub> (c), Ag<sub>152</sub> (d), ~Ag<sub>423</sub> (e) and ~Ag<sub>530</sub> (f). The expected elements are seen. The spectra were collected from a drop-cast sample on an ITO plate. Peaks corresponding to Si, Sn, Ca and O are from the substrate.



Fig. 3 HRTEM images of clusters:  $Ag_{55}$  [a],  $\sim Ag_{75}$  [b],  $\sim Ag_{114}$  [c],  $Ag_{152}$  [d],  $\sim Ag_{202}$  [e] and  $\sim Ag_{423}$  [f]. The images show a gradual increase in cluster size from left to right ('a' to 'c' and 'd' to 'f'). Insets in all the images show the size distribution of clusters, which varies from 1.12 to 3.20 nm. Some bigger nanoparticles were also seen, which could have resulted from aggregation upon electron beam irradiation.

Because such clusters are prone to electron beam-induced damage<sup>21</sup> and subsequent core size evolution with increasing electron beam irradiation, a few aggregates and cores of larger sizes are observed in the images. For comparison, TEM images of the Ag@PET nanoparticle are shown in the Fig. S7, ESI.† It has a wide range of sizes from 3 to 8 nm with an average diameter of 4.8 nm.

The optical absorption spectra of clusters of smaller sizes show multiple features corresponding to the distinct transitions between the discrete energy states (Fig. 4 and S8, ESI<sup>†</sup>). In the still smaller regime of Ag<sub>7</sub>,<sup>22</sup> Ag<sub>8</sub> and Ag<sub>9</sub>,<sup>30</sup> Ag<sub>14</sub>,<sup>43</sup> Ag<sub>16</sub>,<sup>44</sup> Ag<sub>32</sub>,<sup>27</sup> Ag<sub>44</sub>,<sup>28</sup> *etc.* many more features are observed. In the case of Ag<sub>7</sub>, two humps corresponding to 550 and 600 nm were observed.<sup>22</sup>

Similarly for Ag<sub>9</sub>, four features at 450, 489, 629 and 886 nm were observed.<sup>30</sup> Multiple features were also observed from the cluster reported by Kitaev.<sup>24</sup> In the magic-numbered glutathione-protected silver clusters,<sup>29</sup> in the bands 2, 6, 9 and 13 separated by polyacrylamide gel electrophoresis (PAGE), distinct optical features are seen. Multiple step-like features were seen in the absence of plasmon in their optical spectra. Recently, Bigoni's group identified Ag<sub>32</sub> by mass spectrometry<sup>27</sup> where we also see the same step-like features along with the absence of plasmon-like absorption, which appear at about 390–430 nm region for water-soluble clusters. The case is similar for the Ag<sub>44</sub> cluster, as reported by Dass *et al.*<sup>28</sup> Surprisingly, compared with other silver clusters, this system shows five pronounced and three weak bands in its optical spectrum.

From the data presented in Fig. 4, we see that as the sizes increase these low energy features disappear and a large oscillator strength accumulates around 450 nm. Smaller clusters show molecule-like properties with discrete energy levels, which are reflected in their optical spectra. The Ag<sub>44</sub> cluster shows five

intense bands along with three weak bands similar to that reported by Harkness et al.28 For Ag55, two distinct features at 450 (2.75) and 550 (2.25) nm (eV) are seen along with a hump at 495 (2.50) nm (eV). In  $\sim$ Ag<sub>75</sub>, the features appear at 475 (2.61) and 630 (1.96) nm (eV) along with a shoulder at 430 (2.88) nm (eV). ~Ag114 shows two features at 464 (2.67) and 540 (2.29) nm (eV). Ag<sub>152</sub>, ~Ag<sub>202</sub>, ~Ag<sub>423</sub>, ~Ag<sub>530</sub> and AgNP show a single peak at 462 (2.68), 460 (2.69), 458 (2.70), 457 (2.71) and 454 (2.73) nm (eV), respectively. The features merge at around  $Ag_{152}$ . All the smaller clusters also show significant absorption in the 3-4 eV (413-310 nm) window, possibly arising from the Ag-thiolate shell protecting the metal core. Note that the Ag-SR thiolate in toluene solutions typically show absorption in the ultraviolet region. At Ag<sub>152</sub> and beyond, only one feature is seen. Beyond this, the peak position shifts only marginally upon increase in cluster size from ~Ag<sub>202</sub> to ~Ag<sub>530</sub>. Because larger clusters, such as  $\sim Ag_{202}$  and beyond, are not pure, their spectra may also have contributions from impure particles. However, from Ag<sub>152</sub> itself, which is atomically precise, the spectra resemble that of Ag nanoparticles protected with PET, whose peak maximum occurs at 462 nm (Fig. S8, ESI<sup>†</sup>). For water-soluble nanoparticles, SPR occurs in the 390-440 nm window, depending on size. Part of the reason for a red-shifted peak in PET-protected particles is the organic shell, and the other reason is the medium surrounding the particles. Surface plasmon resonance is greatly influenced by the dielectric constant of the solvent. In this case, the solvents are organic, which have much lower dielectric constants (toluene = 2.4 at 20  $^{\circ}$ C) than water (80.4 at 20  $^{\circ}$ C). This could be the reason for the plasmon shift of organic soluble nanoparticles, as suggested by the Mie theory.<sup>1,2</sup> The spectra as a function of energy are plotted in Fig. S8, ESI.<sup>†</sup> For more clarity, the peak position is plotted against the reciprocal of diameter (Fig. 5a). The average diameter was taken from the



**Fig. 4** UV/Vis spectra of clusters with wavelength on the *x*-axis. Reading from bottom up:  $Ag_{44}$  [a],  $Ag_{55}$  [b],  $\sim Ag_{75}$  [c],  $\sim Ag_{114}$  [d],  $Ag_{152}$  [e],  $\sim Ag_{202}$  [f],  $\sim Ag_{423}$  [g],  $\sim Ag_{530}$  [h] and AgNPs [i]. The spectra have been shifted vertically for clarity. The spectra show multiple features up to 'd' (namely, eight bands for  $Ag_{44}$ , two energy bands for  $Ag_{55}$  and  $\sim Ag_{114}$ , and three for  $\sim Ag_{75}$ ). But from 'h' to 'i', only a single plasmon-like feature was observed with a small blue shift (*i.e.*, at higher energy).

TEM analysis. It shows an almost linear behavior, in agreement with the spherical shell model.<sup>54–56</sup> Optical absorption spectra of smaller clusters for both gold and silver exhibit multiple features. As the size decreases below 55, as in the case of Ag<sub>44</sub>, Ag<sub>32</sub>, Ag<sub>9</sub>, for example,<sup>27,28,30,31</sup> many more features appear in the spectra, especially in the red region. Many of these transitions have large contributions from the thiolate shell as shown by time-dependent density functional theory (TDDFT) calculations.<sup>57,58</sup> A comparison of the calculated optical spectrum of various clusters suggests a systematic trend for the core-derived transitions.<sup>57,58</sup> In the limit of large cluster sizes, these transitions converge to the plasmon resonance. From a simplistic argument, one can see that as the proportion of ligand-derived states decrease the dipole transition of the core is dominant in the optical absorption spectra. Comparing the spectra of the clusters listed here, it is seen that large optical density, similar to plasmon resonance, appears in the vicinity of Ag<sub>152</sub>. This cluster is expected to have 92 free electrons, whereas metallicity



Fig. 5 A plot of absorption peak positions with respect to the reciprocal of cluster diameter (a). The average core diameter was obtained from the TEM size distribution. Expanded XPS of the Ag3d region of  $Ag_{55}$ ,  $Ag_{152}$ , AgNPs and Ag(i)-thiolate (b).

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is suggested to occur at around 60 atoms in the case of naked gas phase clusters.<sup>12</sup> However, the thiolated cluster systems are not identical to the bulk fcc solid. For some well-characterized clusters of the type Ag<sub>44</sub>, the cage is known to be a Keplerate solid.<sup>26,31</sup> This hollow cage structure is distinctly different from the molecular analogues of the bulk metal, which can result in a variation of the optical absorption spectrum.

Ultraviolet photoelectron spectroscopic studies of these clusters were attempted but nothing significant was observed from that study. X-ray photoelectron spectroscopy gives some good information regarding the valence state of silver. XPS was also used in evaluating the elemental composition of the samples, although this data are not presented here. For consistency in analysis, we collected XPS of four consecutive systems:  $Ag_{55}$ ,  $Ag_{152}$ , AgNPs and Ag(1)-thiolate (Fig. 5b). The  $Ag_{55}$  cluster shows the  $3d_{5/2}$  peak at 368.0 eV, which is close to the Ag-thiolate peak (368.1 eV). This could be because a higher number of Ag(1)s is present as compared with Ag(0). On the other hand, the  $Ag_{152}$  cluster shows a peak at 367.7 eV, which is closer to that of the AgNPs, further suggesting a change in the properties of materials in the  $Ag_{152}$  regime.

There have been several photoelectron spectroscopic investigations regarding the emergence of metallicity in metal clusters.<sup>10,12,59</sup> These are generally discussed in the light of initial and final state effects.<sup>60</sup> Electronic relaxation of the final state and electronic interaction with the support contributing to the additional screening are important factors for determining the final state effect. Intrinsic electronic structure stabilizing the cluster contributes to the initial state effect.60 Whereas systematic energy shifts of the 4f binding energy is observed in supported gold clusters, no such effect is observed in supported silver clusters.<sup>60</sup> The change in ionization energy as well as the increased width of the photoelectron spectra is proportional to 1/R, as suggested by spherical shell model.<sup>54-56</sup> Electronic and geometric effects contribute to changes in the behavior. In the case of supported Ag clusters, no binding energy shift was observed, which may be attributed to the large separation of the 4d and 5s orbitals in comparison with those of gold because of the lack of relativistic contraction for silver.<sup>60</sup> As a consequence, no large redistribution occurs between the s and d orbitals. While this is the case of un-passivated clusters, in the data presented in Fig. 5b we see a small shift in the increased binding energy in clusters and thiolate in comparison with that of the nanoparticles. This is attributable to the large proportion of Ag<sup>+</sup>. However, for Ag<sub>152</sub>, the spectrum is almost identical to that of AgNPs. Thus, while photoemission using the core level is important to distinguish the clusters from bulk for gold, no large difference are seen for silver.<sup>60</sup> The data are consistent for both the monolayer-protected and naked clusters, as shown here.

The present results suggest the emergence of plasmon-like optical absorption around  $Ag_{152}$ . In silver clusters, metallicity is seen at about 60 atoms in photoelectron spectroscopic studies, as mentioned in a previous study.<sup>12</sup> Unlike the case of naked clusters used for photoelectron spectroscopy, the clusters used here are monolayer protected and have distinct cores of smaller dimensions. A cluster with a different ligand (BBS) also shows

the plasmonic feature, which confirms that the emergence of metallicity is the inherent property of the metal. The origin of metallicity is suggested to be around  $Ag_{152}$ , which has a core of 92 atoms and a shell composed of  $Ag_{60}SR_{60}$ .<sup>42</sup>

### Conclusions

In summary, we report the occurrence of a plasmon-like optical absorption feature in silver clusters prepared in solution. A range of clusters with varying nuclearities were synthesised and analysed through MALDI MS. Well-defined TEM with a gradual increase in size were observed. Different ligands were used to understand the silver-thiolate binding chemistry and its influence on the appearance of the plasmon. Based on the emergence of collective electron resonance in the 150 atom regime, we suggest that this is the window where metallicity originates for silver in monolayer-protected clusters.

### Acknowledgements

We thank the Department of Science and Technology, Government of India for constantly supporting our research program on nanomaterials. I. C. Thanks IITM for research fellowship.

### Notes and references

- 1 G. Mie, Ann. Phys., 1908, 330, 377-445.
- 2 C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.*, 2005, **105**, 1025–1102.
- 3 J. Turkevich, P. C. Stevenson and J. Hillier, *Discuss. Faraday* Soc., 1951, 11, 55–75.
- 4 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801–802.
- 5 P. V. Kamat, J. Phys. Chem. B, 2002, 106, 7729-7744.
- 6 I. Chakraborty, T. Udayabhaskararao and T. Pradeep, J. Hazard. Mater., 2012, 211, 396–403.
- 7 I. Chakraborty, U. B. R. Thumu, G. K. Deepesh and T. Pradeep, *J. Mater. Chem. B*, 2013, **1**, 4059–4064.
- 8 A. George, E. S. Shibu, S. M. Maliyekkal, M. S. Bootharaju and T. Pradeep, *ACS Appl. Mater. Interfaces*, 2012, 4, 639–644.
- 9 M. T. Murphy, S. J. Curran, J. K. Webb, H. Menager and B. J. Zych, *Mon. Not. R. Astron. Soc.*, 2007, **376**, 673–681.
- 10 O. Cheshnovsky, K. J. Taylor, J. Conceicao and R. E. Smalley, *Phys. Rev. Lett.*, 1990, **64**, 1785–1788.
- 11 B. v. Issendorff and O. Cheshnovsky, *Annu. Rev. Phys. Chem.*, 2005, **56**, 549–580.
- 12 K. J. Taylor, C. L. Pettiette-Hall, O. Cheshnovsky and R. E. Smalley, *J. Chem. Phys.*, 1992, **96**, 3319–3329.
- T. Andersson, C. Zhang, A. Rosso, I. Bradeanu, S. Legendre, S. E. Canton, M. Tchaplyguine, G. Ohrwall, S. L. Sorensen, S. Svensson, N. Martensson and O. Bjorneholm, *J. Chem. Phys.*, 2011, 134, 094511–094516.
- 14 T. Andersson, C. Zhang, M. Tchaplyguine, S. Svensson, N. Martensson and O. Bjorneholm, *J. Chem. Phys.*, 2012, 136, 204504–204505.
- 15 V. B. Gildenburg, V. A. Kostin and I. A. Pavlichenko, *Phys. Plasmas*, 2011, **18**, 092101–092106.

- 16 K. Höflich, U. Gösele and S. Christiansen, *Phys. Rev. Lett.*, 2009, **103**, 087404.
- 17 V. Senz, T. Fischer, P. Oelßner, J. Tiggesbäumker, J. Stanzel,
  C. Bostedt, H. Thomas, M. Schöffler, L. Foucar, M. Martins,
  J. Neville, M. Neeb, T. Möller, W. Wurth, E. Rühl, R. Dörner,
  H. Schmidt-Böcking, W. Eberhardt, G. Ganteför, R. Treusch,
  P. Radcliffe and K. H. Meiwes-Broer, *Phys. Rev. Lett.*, 2009,
  102, 138303.
- 18 L. F. Chi, M. Hartig, T. Drechsler, T. Schwaack, C. Seidel, H. Fuchs and G. Schmid, *Appl. Phys. A: Mater. Sci. Process.*, 1998, 66, S187–S190.
- 19 H. Moreira, J. Grisolia, N. M. Sangeetha, N. Decorde, C. Farcau, B. Viallet, K. Chen, G. Viau and L. Ressier, *Nanotechnology*, 2013, 24, 095701.
- 20 Y. Shichibu, Y. Negishi, H. Tsunoyama, M. Kanehara, T. Teranishi and T. Tsukuda, *Small*, 2007, **3**, 835–839.
- 21 L. Dhanalakshmi, T. Udayabhaskararao and T. Pradeep, *Chem. Commun.*, 2012, **48**, 859–861.
- 22 T. Udaya Bhaskara Rao and T. Pradeep, *Angew. Chem., Int. Ed.*, 2010, **49**, 3925–3929.
- 23 E. S. Shibu, M. A. H. Muhammed, T. Tsukuda and T. Pradeep, *J. Phys. Chem. C*, 2008, **112**, 12168–12176.
- 24 N. Cathcart and V. Kitaev, J. Phys. Chem. C C, 2010, 114, 16010–16017.
- 25 I. Chakraborty, W. Kurashige, K. Kanehira, L. Gell, H. Häkkinen, Y. Negishi and T. Pradeep, *J. Phys. Chem. Lett.*, 2013, 3351–3355.
- 26 A. Desireddy, B. E. Conn, J. Guo, B. Yoon, R. N. Barnett,
  B. M. Monahan, K. Kirschbaum, W. P. Griffith,
  R. L. Whetten, U. Landman and T. P. Bigioni, *Nature*, 2013,
  501, 399–402.
- 27 J. Guo, S. Kumar, M. Bolan, A. Desireddy, T. P. Bigioni and W. P. Griffith, *Anal. Chem.*, 2012, 84, 5304–5308.
- 28 K. M. Harkness, Y. Tang, A. Dass, J. Pan, N. Kothalawala, V. J. Reddy, D. E. Cliffel, B. Demeler, F. Stellacci, O. M. Bakr and J. A. McLean, *Nanoscale*, 2012, 4, 4269–4274.
- 29 S. Kumar, M. D. Bolan and T. P. Bigioni, J. Am. Chem. Soc., 2010, 132, 13141-13143.
- 30 T. U. B. Rao, B. Nataraju and T. Pradeep, J. Am. Chem. Soc., 2010, 132, 16304–16307.
- 31 H. Yang, Y. Wang, H. Huang, L. Gell, L. Lehtovaara,S. Malola, H. Häkkinen and N. Zheng, *Nat. Commun.*, 2013, 4, 2422.
- 32 M. W. Heaven, A. Dass, P. S. White, K. M. Holt and R. W. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 3754–3755.
- 33 M. Zhu, C. M. Aikens, F. J. Hollander, G. C. Schatz and R. Jin, J. Am. Chem. Soc., 2008, 130, 5883–5885.
- 34 C. Zeng, T. Li, A. Das, N. L. Rosi and R. Jin, J. Am. Chem. Soc., 2013, 135, 10011–10013.
- 35 C. Zeng, H. Qian, T. Li, G. Li, N. L. Rosi, B. Yoon, R. N. Barnett, R. L. Whetten, U. Landman and R. Jin, *Angew. Chem., Int. Ed.*, 2012, **51**, 13114–13118.

- 36 H. Qian, W. T. Eckenhoff, Y. Zhu, T. Pintauer and R. Jin, J. Am. Chem. Soc., 2010, 132, 8280–8281.
- 37 P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell and R. D. Kornberg, *Science*, 2007, **318**, 430–433.
- 38 A. Dass, J. Am. Chem. Soc., 2009, 131, 11666-11667.
- 39 P. R. Nimmala, B. Yoon, R. L. Whetten, U. Landman and A. Dass, *J. Phys. Chem. A*, 2013, **117**, 504–517.
- 40 A. Dass, J. Am. Chem. Soc., 2011, 133, 19259-19261.
- 41 H. Qian, Y. Zhu and R. Jin, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 696–700.
- 42 I. Chakraborty, A. Govindarajan, J. Erusappan, A. Ghosh, T. Pradeep, B. Yoon, R. L. Whetten and U. Landman, *Nano Lett.*, 2012, 12, 5861–5866.
- 43 H. Yang, J. Lei, B. Wu, Y. Wang, M. Zhou, A. Xia, L. Zheng and N. Zheng, *Chem. Commun.*, 2013, **49**, 300–302.
- 44 H. Yang, Y. Wang and N. Zheng, *Nanoscale*, 2013, 5, 2674–2677.
- 45 K. S. Sugi, I. Chakraborty, T. Udayabhaskararao,
  J. S. Mohanty and T. Pradeep, *Part. Part. Syst. Charact.*, 2013, 30, 241–243.
- 46 I. Chakraborty, T. Udayabhaskararao and T. Pradeep, *Chem. Commun.*, 2012, **48**, 6788–6790.
- 47 S. Knoppe, A. C. Dharmaratne, E. Schreiner, A. Dass and T. Bürgi, *J. Am. Chem. Soc.*, 2010, **132**, 16783–16789.
- 48 A. Dass, A. Stevenson, G. R. Dubay, J. B. Tracy and R. W. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 5940–5946.
- 49 Y. Negishi, R. Arai, Y. Niihori and T. Tsukuda, *Chem. Commun.*, 2011, **47**, 5693–5695.
- 50 Y. Negishi, C. Sakamoto, T. Ohyama and T. Tsukuda, *J. Phys. Chem. Lett.*, 2012, **3**, 1624–1628.
- 51 K. Chaudhari, P. L. Xavier and T. Pradeep, *ACS Nano*, 2011, 5, 8816–8827.
- 52 A. Mathew, P. R. Sajanlal and T. Pradeep, J. Mater. Chem., 2011, 21, 11205–11212.
- 53 J. S. Mohanty, P. L. Xavier, K. Chaudhari, M. S. Bootharaju, N. Goswami, S. K. Pal and T. Pradeep, *Nanoscale*, 2012, 4, 4255–4262.
- 54 R. B. Wyrwas, M. M. Alvarez, J. T. Khoury, R. C. Price, T. G. Schaaff and R. L. Whetten, *Eur. Phys. J. D*, 2007, 43, 91–95.
- 55 O. Varnavski, G. Ramakrishna, J. Kim, D. Lee and T. Goodson, *J. Am. Chem. Soc.*, 2009, **132**, 16–17.
- 56 W. A. de Heer, Rev. Mod. Phys., 1993, 65, 611-676.
- 57 H. Hakkinen, Chem. Soc. Rev., 2008, 37, 1847-1859.
- 58 H. Hakkinen, Nat. Chem., 2012, 4, 443-455.
- 59 I. B. von and O. Cheshnovsky, Annu. Rev. Phys. Chem., 2005, 56, 549–580.
- 60 S. Peters, S. Peredkov, M. Neeb, W. Eberhardt and M. Al-Hada, *Surf. Sci.*, 2013, **608**, 129–134.