The Response of Citrate Functionalised Gold and Silver Nanoparticles to the Addition of Heavy Metal Ions

Short running title: Interactions between metal ions and citrate functionalised nanoparticles of different nanomaterials

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Abstract

Hypothesis

Citrate functionalised gold nanoparticles (AuNPs) have been shown to be effective heavy metal sensors, as their optical spectra quantitatively shifts upon metal-citrate interaction. The speciation and molecular orientation of citrate molecules absorbed on the surfaces of bulk materials is found to be dependent on the substrate material used. It is expected that substituting gold for another nanomaterial should give the citrate molecules at the surface different speciation and molecular orientation, thus providing different citrate/metal interactions and responses.

Experimental

Citrate functionalised AuNP, and AgNP solutions were synthesised for comparison, and characterised before and after the addition of heavy metal ions. This study concentrated on the molecular interactions of the citrate molecules with the nanomaterial surface and the metal ions in solution. Computational simulations into these interactions were also carried out as a comparison.

Findings

The citrate speciation for the AuNPs and AgNPs was significantly different, showing single and double carboxylate coordinated molecules respectively. There were also differences in the heavy metal/citrate interaction. Notably, Pb^{2+} ions produced a rapid coagulation of the AuNPs which was not observed when using AgNPs, demonstrating that the noble metal nanomaterial used has an effect on the nature of the heavy metal/citrate bonding interactions.

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[1] Gold nanoparticles (AuNPs), silver nanoparticles (AgNPs), localised surface plasmon resonance (LSPR), Ultraviolet/Visible absorption spectroscopy (UV-Vis absorption spectroscopy), Transmission electron microscopy (TEM), photon correlation spectroscopy, attenuated total reflectance Fourier transform infrared (ATR-FTIR),

Key words: Citrate functionalised nanoparticles, gold nanoparticle, silver nanoparticles, heavy metals.

1. Introduction

Au and Ag NPs are two of the most widely studied NPs, with applications being found within such fields as: Chemical and biological sensing, catalysts, electronics and photonics,[1-9] all of which make use of the applications of localised surface plasmon resonance (LSPR).[10,11] LSPR is the coherent oscillation of free electrons at the surfaces of the NPs and is spectrally observed as an intense absorbance maximum in the visible part of the electromagnetic spectrum.[10,11]

The synthesis of Au and Ag NPs is usually carried out using a citrate reduction method known as the Turkevich method, with further adaptations of this procedure being studied all the time.[12-16] This popularity is due to its simplicity and reliability for producing controlled, monodispersed NPs, coated with surface-bound citrate molecules as stabilising capping agents.[17-18] Citrate molecules are also valuable precursors for the production of more complex surface-functionalised nanomaterials, due to the ease at which they can be exchanged for other surface molecules.[19,20]

The speciation and orientation of surface-bound citrate molecules has been studied extensively for surfaces, and in recent years, nanoparticles.[21-24] It has been found that citrate ions can adopt unique binding modes, orientations and speciation when deposited on different materials (e.g. Au, Ag, α-FeOOH and TiO_2).[21-26] It has also been discovered that these properties are also dependent on the dimensions the material i.e. thin film or NP.[21-26] This can have a profound effect on the properties of the citrate molecules: A study by Mudunkotuwa et al. has shown that citrate molecules on the surface of TiO2 NPs possess a different speciation, relative to aqueous citrate molecules.[21] At pH 2, the carboxyl groups and hydroxyl group of free aqueous citrate molecules are completely protonated. In contrast, the molecular spectra for the surface-bound citrate molecules suggested that the carboxyl groups of the citrate molecules were deprotonated. This was attributed to a change in the pKa values for the carboxylate groups upon surface binding to the TiO_2 NPs.

The carboxyl and hydroxyl groups of citrate ions have a natural affinity for divalent metal ions, with many metal-citrates being synthesised.[27-30] This affinity has also made citrate functionalised NPs a target in the development of chemical nanosensors.[31-33] Changing the chemical properties of the surface-bound citrate molecule inherently affect its interactions with surrounding ions. An example of this difference in metal-citrate speciation, for free and surface-bound citrate molecules, would be to look at the reaction between Cu^{2+} ions and aqueous citrate molecules in solution: A solution of free citrate molecules, at a pH between 5.5 – 7.4, are found to react with Cu^{2+} ions, resulting in a reduction in the pH of the solution; whereas, between pH 6.0 – 8.0, a drop in pH on reacting with Cu^{2+} ions have not been observed with citrate functionalised AuNPs.[33,34] This fundamental uncertainty means an assumption cannot be made that free aqueous and surface-bound citrate molecules will have the same properties, or will interact with the surrounding medium in the same way.

This study looks at the different binding modes, orientations and speciation of citrate molecules on the surfaces of 6 nm AuNPs and 4-5 nm AgNPs. The effects of the NP materials on the functionality of the surface-bound citrate molecules will also be studied, by comparing the citrate-metal interactions in a solution of aqueous Pb^{2+}, $Cd^{2+,}$ Ni^{2+}, and Hg^{2+} ions. We employ ATR-FTIR to obtain molecular spectroscopic data, zeta-potential measurements for surface charge and NP stability analysis, photon correlation spectroscopy (PCS), and transmission electron microscopy (TEM) to characterise the size of the particles. We further employ computational modelling to try to understand the different binding modes, orientations and species involved in these complex systems, and the effects on changing the material of the NPs. The principles of altering the chemical properties of functional surface molecules, demonstrated in this work, clearly have vast applications in areas such as chemical sensing, chemical filtration, metal ion scavenging etc.

Experimental Methods

Materials. Au(III) chloride trihydrate was used as a source of gold atoms, silver nitrate ($AgNO_3$) was used as a source of Ag atoms, and trisodium citrate dihydrate as a source of citrate molecules (Sigma-Aldrich, UK). Standard heavy metal solutions were produced using the following chemicals: $Pb(NO_3)_2$ (ASC >99.0%), $CdCl_2$ (Technical Grade), $NiCl_2$ (98%) and $HgCl_2$ (99.5%); all of which were obtained from Sigma-Aldrich, UK.

Metal ion/NP Solutions. Stock solutions of all of the metal ions were made with metal ion concentrations of 3.81×10^{-4} M. These metal solutions, or their dilutions, were added to the NP solutions as a 1 to 1 volume ratio.

Synthesis of Citrate Functionalised AuNPs. AuNPs were prepared by the standard Turkevich method, which involves reduction of gold chloride using sodium citrate.[12] 105 mL of water was heated to boiling in a 250 ml conical flask. The water was removed from the heat and trisodium citrate (61.7 mg) was added. 1 ml aqueous solution of $HAuCl_4.3H_2O$ (9.9 mg) was then added to the citrate solution and left for 15 min whilst stirring.

Synthesis of Citrate Functionalised AgNPs. The AgNP solution was prepared by using the citrate reduction method based on that of Lee and Meisel.[37] All solutions were prepared in deionised water. 50 ml of $1\cdot10^{-3}$ M $AgNO_3$ was heated to boiling. To this solution 5 ml of a 58.7 mg trisodium citrate dihydrate solution was added dropwise and stirred vigorously. The solution was heated until it became pale yellow. Then it was removed from the heat and stirred until it had cooled to room temperature. The solution was then made up to 105.7 ml to keep the citrate concentration equal in both the AuNP and AgNP solutions.

Qualitative Characterisation of NP and Metal ion/NP solutions. Uv-Vis absorption spectroscopy was carried out, using a Perkin Elmer Lambda 40 UV-Vis Spectrometer, to determine the LSPR absorption maximums of the NP and metal ion/NP solutions. Deionised water was used as a blank sample. AuNP and AgNP sizes were measured using PCS and TEM imaging.

Metal Ion Induced Aggregation Measurements. PCS measurements were obtained to estimate the size of the particles in solution. These measurements were carried out using a Malvern Zetasizer nano ZS (633nm He-Ne laser, maximum power 5mW) which estimated the particle diameters by dynamic light scattering. Zeta potential measurements were made using a Malvern Zetasizer nano ZS instrument using a zeta potential cell.

Measurement of Metal Ion Induced pH Changes. Studies into the resultant pH of the metal ion/AuNP and metal ion/AgNP solutions were carried out to note any pH changes during the metal-citrate complex formation. Monitoring the pH of the sample solutions was done using a pH meter (Hanna Instruments pH 209) and a pH electrode system. This system was calibrated using two separate buffer solutions of pH 7 and pH 4.

ATR-FTIR Spectroscopy. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to obtain vibrational spectra of the surface citrate and metal citrate species present on the AuNP and AgNP surfaces. Solutions were added as a single 20 µL drop onto a glass slide and allowed to dry in air. A blank ATR-FTIR sample spectrum was obtained for a clean glass slide and then the spectra were recorded for the NP and metal ion/NP samples with a Thermoscientific Nicolet iS5 FTIR iD5 ATR.

Computational IR Spectroscopy Predictions. Theoretical calculations of the IR spectra for the surface‑citrate molecules, and for the metal ions bound to the surface-citrate molecules, were carried out using a semiempirical PM6 method by using MO-G as part of the SCIGRESS program.[35,36] To simulate the surface of the Au and Ag NPs a 3x3x2 crystal lattice, consisting of the respective metal atoms was created. These atoms were then locked at their geometrical coordinates so that the sheet would not deform during geometrical optimization. Citrate molecules were then added to the surface by one or two of the carboxylate groups. Before the IR spectral were calculated, all of the chemical structures were geometrically optimised by a molecular mechanics method (MM2). To explore the interactions between metal ions in solution and the citrate-coated surface of a AuNP or AgNP, the divalent metal ion under study was placed in close proximity to the surface-bound citrate molecule and a further geometric optimization was carried out. The IR data obtained was plotted as the energy of the transition (in cm^{-1}) against Transmission (%). A band Guassian broadening of 100 cm^{-1} was applied to each data point to produce spectra more representative of the experimental data obtained.

Results and Discussion

UV-Vis Absorption Spectroscopy. The AuNP and AgNP solutions prepared by the citrate reduction method displayed characteristic absorption spectra with LSPR absorbance maxima at values of 525 nm and 415 nm respectively (Figures 1 and 2). When the NP solutions contained Ni^{2+}, Cd^{2+}, Hg^{2+}, or Pb^{2+} ions (1.905×10^{-4} M), there was a shift in the LSPR band. This indicates that the metal ions were interacting with the surfaces of the AuNPs and AgNPs affecting the local refractive index at the surfaces of the NPs.[37,38]

The Pb^{2+}/AuNP solution was the only sample to display two LSPR absorbance maxima at 528 nm and 633 nm. The LSPR band at 528 nm had red-shifted by 3 nm, relative to the LSPR band of the AuNP solution and is present as a result of Pb-citrate interactions at the surface of the AuNPs. TEM and PCS analysis confirmed that the peak centred at 628 nm was due to plasmon-coupling, induced by the aggregation of the AuNPs (Figure 3 and Table 1). Additionally, 15 minutes after mixing, the Pb^{2+}/AuNP solution turned from red to blue and finally clear. A blue AuNP solution is another known feature of plasmon coupling.[39] On reducing the Pb^{2+} ion concentration to 1.207×10^{-7} M, the solution remained red and the 633 nm absorbance maximum was no longer present. This shows that the observed results are dependent on the concentration of Pb^{2+} ions in solution. Solutions containing larger AuNPs also became clear with a Pb^{2+} ion concentration of 1.905×10^{-4} M and in these solutions, aggregates of AuNPs could clearly be seen. All of the other metal ion/AuNP solutions remained red, and the spectra exhibited no signs of plasmon coupling.

In contrast, the Pb^{2+}/AgNP solution did not display any plasmon coupling effects although, after 24 hours, all of the metal ion/AgNP solutions developed a band of colour in the lower portion of the solution. This is due to sedimentation, representative of the destabilisation of the AgNPs, but not at a significant level to cause aggregation and plasmon coupling. Interestingly, the Hg^{2+}/AgNP solution shows a relatively large blue-shift of the LSPR band by ~268 nm. This is spectral shift is indicative of the formation of a Hg-Ag amalgam, shifting the LSPR absorbance maximum to a lower wavelength. [43,44]

Nanoparticle Stability. Diameter measurements of the AuNPs and AgNPs by PCS were comparable to those obtained by TEM imaging (Figure 3 and Table 1). All of the metal ion/NP solutions were shown to have increased particle sizes, compared to the AuNP and AgNP solutions. The Pb^{2+}/AuNP solution was the only sample that showed the presence of particles >200 nm due to mass aggregation. The other metal ion/AuNP solutions showed size increases of between 10 nm and 12 nm, and size increases of 5 nm to 17 nm for the metal ion/AgNP solutions.

Derjaguin, Lindau, Verwey and Overbeek (DLVO) theory states that the stability of a colloidal system is determined by the sum of the van der Waals attractive forces and the electrical double layer forces present between the NPs as they approach each other.[40] Theoretically, a stable surface charge is defined as either ± 40 mV, which provides enough NP-NP repulsion to prevent aggregation. The negatively charged carboxylate groups of the surface bound citrate molecules provided enough repulsion between the negatively charged NPs to stop them from aggregating instantly. In solution, divalent metal ions can bind with free citrate molecules via the carboxylate groups and the hydroxyl group. Binding between the metal ions in solution and the carboxylate groups of the citrate molecules would reduce the repulsive surface charges of the NPs, increasing aggregation. The AuNP solution was theoretically stable, with a measured surface charge of <-40 mV (Table 1.). This charge became more positive upon the addition of Ni^{2+}, Cd^{2+}, Hg^{2+}, or Pb^{2+} ions. The Ni^{2+}, Cd^{2+}, and Hg^{2+} metal ion/AuNP solutions showed a similar reduction in surface charge (~+4.30 mV), but the Pb^{2+}/AuNP solution underwent a much larger reduction (+43.2 mV) (Figure 4). Bringing the surface charge close to neutral resulted in a significantly destabilised NP solution, explaining the observed aggregation of the AuNPs.

Notably, the surface charge of the AuNPs was more than twice as negative as that of the AgNPs. With a surface charge less than ± 40 mV, the AgNP solution was theoretically unstable. This would explain the appearance of a coloured band in the metal ion/AgNP and AgNP solutions as there was less NP-NP repulsion, bringing the NPs closer together. The introduction of Pb^{2+}, Cd^{2+}, or Ni^{2+} ions to the AgNP solution resulted in a reduction in the surface charge of between +0.3 to +2.9 mV. In contrast, Hg^{2+}/AgNP solution was the only metal ion/AgNP solution to show an increase in the surface charge (-0.9 mV).

Solution pH measurements. The Pb^{2+}/AuNP solution also displayed a relatively large reduction in the pH of the solution, by -5.3 units. All of the other metal ion/AuNP solutions remained in the 5.1 – 7.5 pH range (Figure 5). The pH of the metal ion/AgNP solutions dropped by between 0.4 - 0.5 units, except for Ni^{2+} which decreased by 0.9 units. The large pH decrease for the Pb^{2+}/AuNP solution is an important finding, as at low pH values the positively charged protons in the solution gather around the negatively charged NPs reducing the surface charges. Therefore, it cannot be said that the destabilization of the AuNPs was solely due to the Pb^{2+} ions interacting with the citrate molecules on the surface if the AuNPs. This is reflected in the relationship between the size distribution of the NPs in the metal ion/NP solutions and the pH of the solution (Figure 5).

The carboxylate groups of free citrate molecules in solution are fully protonated at pH ~ < 3 . Mudunkotuwa *et.al* has shown that the carboxylate groups of the citrate molecules on the surface of 4 nm TiO_2 NPs do not become protonated at low pH.[21] If this is true for the AuNP solutions, the reduction in the surface charge will be from Pb^{2+}-citrate binding and the increase in protons at the NP surfaces, rather than the protonation of the carboxylate groups of the citrate molecules.

The change in pH, surface charge, and the subsequent effects of plasmon coupling were dependent on the concentration of the Pb^{2+} ions. On reducing the concentration of Pb^{2+} ions by half, the pH decreased to 4.8 and plasmon coupling effects were not observed. A timed study was carried out into the pH decrease of this Pb^{2+}/AuNP solution. During the first minute there was a relatively sharp decrease in pH (-0.9 units). Over a 14 minute period the solution pH continued to decrease to a pH of 4.87. The pH of the solution remained at 4.87 for a further 30 minutes. After a 24 hour period the solution pH had decreased further to 4.58. A graph of (1/pH) versus time produced a linear plot (R^2 = 0.98) from 4 to 15 minutes, signifying a second order reaction rate. On doubling the Pb^{2+} ion concentration, the rate of the reaction quadrupled, which is also characteristic of a second order reaction. The data between 0 - 4 minutes and for >30 minutes was nonlinear with respect to (1/pH) versus time. This data indicates the existence of at least three transitional reactions taking place. A similar three-step reaction path has been noted for the interaction of

Cu^{2+} ions with free citrate molecules in solution;[41] although, it has not been found in the literature, that Pb^{2+} ions react with unbound citrate molecules in this way. These observations further demonstrate the lack of predictability when comparing the formation of metal-citrate species using metal ions and unbound citrate molecules, and metal ions with the citrate molecules on the surface of NPs. This lack of predictability can also be extended to metal ion interactions between surface-citrate molecules bound to different nanomaterials as the Pb^{2+}/AgNP solution showed relatively little pH change compared to the Pb^{2+}/AuNP solution.

Comparison between ATR-FTIR spectroscopy and Theoretical Predictions. ATR-FTIR spectra of the AuNPs and AgNPs displayed an intense band positioned respectively at 1393 cm^{-1} and 1353 cm^{-1}, resulting from the symmetric stretching of the carboxylate groups of the citrate molecules ($\nu_s(COO^-)$) (Figure 6). The band positions are different than that of the literature value for free citrate molecules (1417 cm^{-1}), indicating that the citrate molecules are bound to the surfaces of the AuNPs and AgNPs.[42] These bands also show the presence of two shoulders which are attributed to the non-equivalent environments of the three carboxylate groups. The O-H stretch mode of the hydroxyl group (ν(O-H)) is present as a broad peak, centred at 3310 cm^{-1} (AuNPs) and 3382 cm^{-1} (AgNPs). Additionally, the AuNPs displayed a weak band centred at 1298 cm^{-1}, corresponding to rotation of an unbound hydroxyl group.[22] As this band is absent from the AR-FTIR spectrum for the AgNP solution, this could indicate that the hydroxyl group of the surface citrate molecules is bound to the surface of the AgNPs.[22]

The most notable difference in the ATR-FTIR spectra is that the intense band of the asymmetric carboxylate stretch ($\nu_{as}(COO^-)$) (~1580 cm^{-1}) is absent from the

AgNP sample. This suggests that the asymmetric carboxylate stretch is parallel to the surface of the AgNPs, resulting in an infrared inactive transition.[24] This indicates that multiple carboxylate groups of the citrate molecules, are attached to the surface of the AgNPs. The ATR-FTIR spectrum for the AuNPs sample does show an intense band attributed to the asymmetric carboxylate stretch. This indicates that the citrate molecules are bound to the surfaces of the AuNPs by single carboxylate groups.

These observations are complimented by computational simulations for the structure of the surface-bound citrate molecules on Au and Ag surfaces, and the resultant IR spectra. After geometric optimisation, the calculated IR spectra closely matched the experimental ATR-FTIR spectrum for the AuNP and AgNP samples (Figure 7). The simulated IR spectrum for the surface citrate molecule bound by a single carboxylate group has two intense bands, which are attributed to the symmetric and asymmetric carboxylate stretches. The simulated spectrum for the surface citrate molecule bound by two carboxylate groups to a Ag surface, only contains the band associated with the asymmetric carboxylate stretch.

The geometrically optimised citrate conformations can also help explain why the AuNPs had a more negatively charged surface, relative to the AgNPs (Figure 7 insert): As two carboxylate groups of each surface-bound citrate molecule are bound to the surface of the AgNP, only one carboxylate group from each surface-bound citrate molecule is free to contribute to the negative surface charge; In contrast, as only one carboxylate group is bound to the surface of the AuNP, two unbound carboxylate groups from each surface-bound citrate molecule can contribute charge. This leads to a greater contribution of negative charges from the citrate molecules on the surfaces of the AuNPs, relative to the AgNPs.

ATR-FTIR spectra for the metal ion/AuNP and metal ion/AgNP solutions demonstrate the differences in the metal-citrate speciation by the peaks present for the carboxylate groups (Figure 8 and 9). The symmetric and asymmetric carboxylate stretches are still present for the metal ion/AuNP solutions and the symmetric carboxylate stretches are still present for the metal ion/AgNP solutions. The variances in the intensities of these bands show an expected interaction between the metal ions and the carboxylate groups of the surface-bound citrate molecules.

Computational simulations into the potential metal-citrate structures that are formed at a Au surface, produced unique structures for each metal ion (Figure 10). Cd^{2+}, Ni^{2+} and Hg^{2+} ions formed metal-citrate structures where the Au surfaces retained their negative net charge, due to the unbound carboxylate groups. The Ni^{2+} ion was weakly bound to two carboxylate groups via a double bonded oxygen atom, and a negatively charge single bonded oxygen atom, with a third Ni-O bond to the hydroxyl group. This resulted in a charge contribution of -1 from the citrate molecule. A Cd^{2+} ion was predicted to be weakly bound to two carboxylate groups via the double bonded oxygens, leaving the two negative charges of the carboxylate groups intact. Surprisingly, the Hg^{2+} ion did not bind to the citrate molecule, thus leaving the original net charge from the two unbound carboxylate groups of the citrate molecule. As experimental measurements show, there is a slight reduction in the surface charge of the AuNPs upon the addition of Cd^{2+}, Ni^{2+} or Hg^{2+} ions. This shows that there is still a charge contribution from unbound carboxylate groups, which is in agreement with the computational data. The predicted structures for the binding of a Pb^{2+} ion with the surface-bound citrate molecules suggested that the two unbound carboxylate groups were involved in bonding, reducing the charge contribution from the citrate molecule to 0. This prediction is comparable with the experimental values for the surface charge of the AuNPs in the Pb^{2+}/AuNP sample, where the surface charge had considerably reduced.

Computational studies also predicted that the metal/citrate molecules formed at the Ag surface, with Cd^{2+}, Ni^{2+} and Hg^{2+} ions, would produce structures that retained their negative surface charge. For Cd^{2+} and Ni^{2+}, the metal ion only bonded with the two already bound carboxylate groups and the Ag surface and the Hg^{2+} ion only bound to the Ag surface (Figure 11). Experimental results are in good agreement with this as there was very little change in the surface charge of the AgNPs. In contrast, simulations showed that the Pb^{2+} ion interacted with the unbound carboxylate group cancelling the negative charge of the surface citrate molecule. This is not shown in the experimental data, in which the surface charge of the Pb^{2+}/AgNPs is comparable to that of the AgNPs.

ATR-FTIR spectroscopy showed that the intensity of the ν(O-H) band varied with different metal ion/NP solutions. Most notably, the ν(O-H) band intensity for the Pb^{2+}/AuNP solution had decreased more than any other sample tested here. Assuming that all of the carboxylate groups are deprotonated, the only other proton source from is from the hydroxyl group of the surface citrate molecules. Therefore, it is possible that the large decrease in the pH of the Pb^{2+}/AuNP solution is due to the loss of a proton from the hydroxyl group – shown by the reduced ν(O-H) band intensity.[25,26] In comparison, the Pb^{2+}/AgNP solution shows a relatively small reduction in the pH of the solution and the spectrum maintains the ν(O-H) band intensity. Theoretical results showed a weakening of the O-H bond of the citrate molecule bound to a Au surface, after the addition of a metal ion. This is probably due to the electron-withdrawing properties of the metal ions, which will draw electron density from the molecule, reducing the electron density at the O-H bond. Although, in the computational calculations predicted that the Pb^{2+} ion actually produces the most stable O-H bond relative to the other ions studied here.

Conclusion

Citrate functionalised Au and Ag nanoparticles were successfully prepared by a citrate reduction method. The optical properties (UV-Vis absorption spectroscopy and ATR-FTIR), particle size (TEM and PCS), surface charge, and the pH value of the solutions were then monitored as different metal ion/NP solutions were prepared. These measurements showed that all of the metal ions interacted with the surfaces of the NPs. Notably, the most dramatic effects came from the Pb^{2+} ion interaction with the surface-bound citrate molecules of the AuNPs, resulting in a large decrease in the pH, a reduced surface charge, and the resultant aggregation of the AuNPs. It was found that changing the NP material from Au to Ag had a significant effect on the conformational bonding of the surface-citrate molecules to the surfaces of the NPs. This was observed through the ATR-FTIR spectrum for the NPs, which had completely different spectra. This variation in the surface-citrate binding modes affected the Au and Ag NP surface charges and resultantly the differences in metal-citrate speciation. This effect clearly displays that the interaction of a metal ion with surface-bound citrate molecules on different material NPs, cannot be assumed to be identical. This further leads to different metal-citrate interactions at the surfaces of the NPs, and unique metal-citrate complexes. This was backed up by computational results, which provided unique metal-citrate complexes at the Au and Ag surfaces.

This study clearly shows that the properties of functional surface molecules can be altered by changing the surface composition of a nanomaterial. Here, this process changed the interaction between the surface-citrate molecules and the metal ions in solution. The significance of these results lie in demonstrating the possibilities of altering the properties of currently employed functional molecules for further uses, potentially enhancing the usability of the functional molecules, or altering the natural affinity for specific target chemicals. Obvious possibilities include applications within nanosensors, chemical filtration and scavenging etc., all of which are current areas of intense research interest. The authors hope that the principles studied here will add to the research into the additional uses of currently employed functional molecules, further enhancing the tuning capabilities of nanomaterials, for specific functionalities.

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Table 1 Diameter estimation by PCS and TEM, surface charge, and pH of the AuNP and AgNP solutions in the presence of Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions (1.905×10^{-4} M) metal ion concentration, 24 hours after mixing.

NP Sample	**Metal ion**	**Metal Concentration in NP Solution (M)**	**pH**	**Zeta Potential (mV)**	**Particle Size (Estimated by PCS) (nm)**	**Particle Size Taken from TEM (nm)**
AuNP	-	-	6.3	- 44.3	6	6
	Pb^{2+}	1.905×10^{-4}	1.0	-1.1	>200	
	Cd^{2+}	1.905×10^{-4}	7.4	~ (- 40)	16	
	Ni^{2+}	1.905×10^{-4}	7.5	~ (- 40)	18	
	Hg^{2+}	1.905×10^{-4}	6.7	~ (- 40)	18	
AgNP	-	-	6.0	-16.6	3	4-5
	Pb^{2+}	1.905×10^{-4}	5.5	- 15.7	16	
	Cd^{2+}	1.905×10^{-4}	5.6	- 13.5	15	
	Ni^{2+}	1.905×10^{-4}	5.1	-16.3	20	
	Hg^{2+}	1.905×10^{-4}	5.5	-17.5	8	

FIGURE LEGENDS

Fig.1 UV-Vis absorption spectra for AuNP and metal ion/AuNP solutions, showing the various shifts in the plasmon band absorbance maximums due to the interaction of the metal ions with the surfaces of the NPs.

Fig. 2 UV-Vis absorption spectra for AgNP and metal ion/AgNP solutions showing the various shifts in the plasmon band absorbance maximums due to the interaction of the metal ions with the surfaces of the NPs.

Fig. 3 TEM images for the (left) AuNP and (right) AgNP solutions.

Fig. 4 The estimated diameters of the Au and Ag NPs compared to particle surface charge for metal ion/AuNP and metal ion/AgNP solutions (Pb^{2+} has been removed because of scaling to allow a more detailed analysis of the other metal ion/NP solutions).

Fig. 5 A Graph showing the particle sizes measured by PCS, against the change in pH of the metal/NP solutions.

Fig. 6 ATR-FTIR spectra for the surface citrate molecules for the AuNP and AgNP solutions highlighting the main variance is the absence of the intense band of the asymmetric carboxylate stretch ($\nu_{as}(COO^-)$) (~1580 cm^{-1}) from the AgNP sample. This suggests that the citrate molecules are bound to the AgNP surfaces via several carboxylate groups.

Fig. 7 The simulated IR spectra for a surface-citrate molecule bound to a surface via a single carboxylate group (transitions marked with★) and for a surface-citrate molecule bound to a surface via two carboxylate groups (transitions marked with ■). The insert shows the predicted surface-bound citrate structure.

Fig. 8 The ATR-FTIR spectra for the metal ion/AuNP solutions, which displayed differences in the carboxylate and hydroxyl related bands.

Fig. 9 ATR-FTIR spectra for the metal ion/AgNP solutions that displayed differences in the carboxylate and hydroxyl related bands.

Fig. 10 The Predicted conformations of the metal-citrate molecules formed at a Au surface, with the different divalent metal ions studied here: (A) Ni^{2+} (B) Cd^{2+}, (C) Hg^{2+}, and (D) Pb^{2+}.

Fig. 11 The Predicted conformations of the metal-citrate molecules formed at a Ag surface, with the different divalent metal ions studied here: (A) Pb^{2+} (B) Ni^{2+}, (C) Cd^{2+}, and (D) Hg^{2+}.

Biographies:

Mark Frost is now studying for his PhD at Manchester Metropolitan University with a research interest in the production nanomaterials and their employment into heavy metal ion sensors.

Michael Dempsey is an applied microbiologist with an interest in water and waste-water treatment. Inventor of improvements to expanded and fluidized bed biofilmreactor technology. He is also the Head of Faculty Research Degrees and Head of Faculty Centre for Postgraduate and Early Career Researchers.

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