Effect of halogen addition to monolayer protected gold nanoparticles†

Sanjay Singh,[a] **Renu Pasricha,**[a] **Umananda M. Bhatta,**[b] **P. V. Satyam,**[b] **Murali Sastry‡**[a] **and B. L. V. Prasad***[a]

The effects of *N*-halosuccinimide and halogen addition to monolayer protected gold nanoparticles (Au NPs) dispersed in organic media are described. Contrary to the expectation that nanoparticles dispersed in organic media are stable against aggregation, *N*-iodosuccinimide addition induced aggregation of octadecylamine capped gold nanoparticles in chloroform or toluene. It was observed that even KI and CuI addition could bring about the aggregation though they are very sparingly soluble in organic solvents. It was also found that even molecular iodine could bring about the above mentioned aggregation. Interestingly, when CuI is used the aggregated structures readily convert to very thin flat nanostructures upon exposure to an electron beam or UV irradiation. In fact when the aggregation is induced by the addition of KI or *N*-iodosuccinamide we do not see the flattening of the aggregated structures exemplifying the important role of Cu ions in making these flat structures.

Introduction

A very important attribute of coinage metal nanoparticles like gold, silver and copper is their colour arising due to the collective oscillation of induced dipoles in resonance with the incident electromagnetic radiation.[1] The interesting part of this property is its dependence on the particle size, shape and the nature of the surrounding medium.[2] The influence of the latter two is in general greater than that of size. An exciting feature of the optical properties of anisotropic or aggregated gold nanoparticles is the appearance of the absorbance peak in the near infra-red (NIR) region. Because of the transparency of biological cells in this region this property of the anisotropic particles has gained attention for many biological applications including cancer hyperthermia.[3] Another interesting technical application of the anisotropic or even aggregated particles is for architectural purposes where the near-infrared absorbing particles could be used for optical coatings.[4]

While there is abundant literature on the synthesis of anisotropic nanoparticles[5] a sizeable section of literature in the area of metal nanoparticles is also devoted to devising scaffolds to obtain controlled aggregates forming nanoparticle networks.[6] This is perceived to be a very important step for devices based on nanoparticles for sensors, catalysts and electronic applications. In this context there have been sporadic reports of the aggregation and annealing of spherical nanoparticles into anisotropic structures.[7]

In colloid chemistry the stability of charged particles in aqueous solutions is probably the most studied phenomenon. This is known to rely on the exquisite balance of the electrostatic repulsion and van der Waals attractive forces between the charged particles that crucially depend on the ionic strength of the fluid as explained by the DLVO theory.[8] Thus it becomes obvious that addition of ions can decrease the electrostatic repulsion and bring about aggregation of nanoparticles. However, in organic media it is normally the steric repulsions between the capped organic molecules that prevent the aggregation of nanoparticles and it is generally assumed that these dispersions are stable against aggregation[9] unless a bifunctional molecule that could replace the existing capping molecule and link the two nanoparticle surfaces is added.[10]

In this paper we show our results that even in nonpolar organic media the stability and size of monolayer protected gold nanoparticles (Au NPs) could be altered by the addition of *N*-halosuccinimides (NCS: *N*-chlorosuccinimide, NBS: *N*-bromosuccinimide, NIS: *N*-iodosuccinimide) or molecular Br$_2$, I$_2$ and even KI and CuI. More specifically we found that aggregation can be induced in octadecylamine (ODA) capped gold nanoparticles dispersed in organic media by the addition of small amounts of NIS, molecular iodine, CuI or KI, though the last two reagents are very sparingly soluble in organic solvents like toluene and CHCl$_3$. Through the addition of molecular iodine we could determine the minimum concentration necessary to bring out the aggregation to be 10^{-6} M. It is hypothesized that in nonpolar organic solvents the reagents added, namely, NIS, CuI and KI could be generating very small quantities of iodine atoms and it is suggested that these are the species responsible for the phenomenon of aggregation. Interestingly addition of Br$_2$ or NBS (which is again known to generate small quantities of Br atoms in nonpolar solvents) did not cause the aggregation though they seem to have changed the shape of the nanoparticles. On the other hand addition of NCS does not have any major effect on the size or shape of the nanoparticles. Another remarkable phenomenon we noticed is that the aggregate structures brought about by CuI addition

[a]Nanoscience Group, Materials Chemistry Division, National Chemical Laboratory, Pune – 411 008, India. E-mail: pl.bhagavatula@ncl.res.in; Fax: +91 20 25902636; Tel: +91 20 25902013
[b]Institute of Physics, Bhubaneswar – 751 005, India
† Electronic supplementary information (ESI) available: UV-Vis spectra of ODA-capped Au NPs after addition of different concentrations of NIS, FTIR spectra of ODA-capped Au NPs before and after addition of NCS, NBS and NIS, FTIR spectra of NCS, NBS and NIS molecules, powder XRD of ODA capped Au NPs and after addition of NCS and NBS, TEM and HRTEM images of the flat structures. See DOI: 10.1039/b614934k
‡ Current address: Tata Chemicals Ltd, Leela Business Park, Andheri (E), Mumbai – 400 059, India.

readily become very thin flat structures upon exposure to an electron beam in an electron microscope or UV irradiation. Careful high resolution transmission electron microscopy (HRTEM) with energy dispersive X-rays reveals that some of these flat structures consist of AuI phases pointing to the interesting chemistry that is happening with the iodide addition to gold nanoparticles. The fact that KI addition or NIS addition fails to bring about this flattening exemplifies the importance of Cu in this process.

We wish to point out here that there have been many reports on the effect of halide ion addition on the shape and size of pre-formed gold nanoparticles as well as their pronounced effect as additives during the synthesis of nanoparticles.[11] However, all the studies present in the literature, to the best of our knowledge, are concerned with aqueous dispersions of nanoparticles and not those dispersed in organic media. The most elaborate studies of them all were by Pileni's group, who delineated the effect of salt addition during the formation of Cu nanoparticles in an isooctane–water system leading to various shapes. They ascribed the results to the differential anion adsorption on the (111) and (100) faces of the fcc lattice.[12] On the other hand this study presents the effect of halogen containing reagents on the pre-formed gold nanoparticles in organic media. The shape changes and/or the aggregation if brought about in the organic media present many advantages such as the compatibility of these structures with polymers. This makes them more amenable to applications such as optical coatings.[4] Presented below are the details of our investigation.

Experimental

Materials

All the chemicals, *viz.* chloroauric acid (HAuCl$_4$·3H$_2$O), sodium borohydride, octadecylamine (ODA), copper iodide (CuI), *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), potassium iodide (KI), bromine and iodine were obtained from Aldrich Chemicals and used as received.

Preparation of gold nanoparticles (Au NPs) and their phase transfer

Choloauric acid (500 mL of 10^{-4} M) was reduced by sodium borohydride (0.05 gm). The solution immediately turned ruby red in colour. This solution was aged for 24 h in order to ensure complete reaction. This solution of gold nanoparticles (500 mL) was taken with 50 mL of 10^{-3} M ODA in chloroform. Vigorous shaking of this mixtures results in the transfer of Au NPs from the aqueous to the chloroform phase and is seen as a transfer of the ruby red colour from water to chloroform. After the completion of phase transfer the organic phase was separated from the aqueous phase. UV-Vis-NIR absorbance spectra were recorded from this solution, which show the appearance of a surface plasmon resonance (SPR) band at about 520 nm, which is a characteristic feature of spherical Au NPs.

With these hydrophobised Au NPs all further experiments were performed. In one typical experiment, 10 mL of hydrophobised Au NPs were treated separately with CuI, and KI under constant stirring and UV-Vis-NIR absorbance spectra were recorded. Both CuI and KI are very sparingly soluble in CHCl$_3$. We added 5 mg of each of the salts to 5 mL of CHCl$_3$. After sonication for 5 minutes the solutions were allowed to settle down for another 5 minutes and 100 μL of the clear supernatant solutions were added to the chloroform dispersion of ODA capped nanoparticles. In another set of experiments, 9 mL of hydrophobised Au NPs (10^{-3} M) were mixed separately with 1 mL of NBS, NCS and NIS (10^{-3} M each) and UV-Vis-NIR absorbance spectra from the resultant mixture were recorded. Similarly 10^{-5} M CHCl$_3$ solutions of molecular bromine and molecular iodine were made and 1 mL each of this solution was added to 9 mL of hydrophobised Au NPs (10^{-3} M) and the UV-Vis-NIR spectroscopic experiments were performed.

Sample characterization

The optical properties of the ODA capped Au NPs in chloroform as well as those treated with CuI, CuBr, KI, NCS, NBS and NIS were monitored on a Jasco V-570 UV/Vis/NIR spectrophotometer operating at a resolution of 2 nm. The FTIR spectra were recorded on a Perkin-Elmer Spectrum One instrument at a resolution of 4 cm^{-1}. Samples for FTIR spectra were prepared by extensive washing of ODA capped Au NPs treated with NBS, NCS and NIS with chloroform, followed by centrifugation, and the precipitate was mixed with KBr to make a pellet, while pure ODA, NBS, NCS and NIS were mixed with KBr to make a pellet and FTIR spectra were recorded.
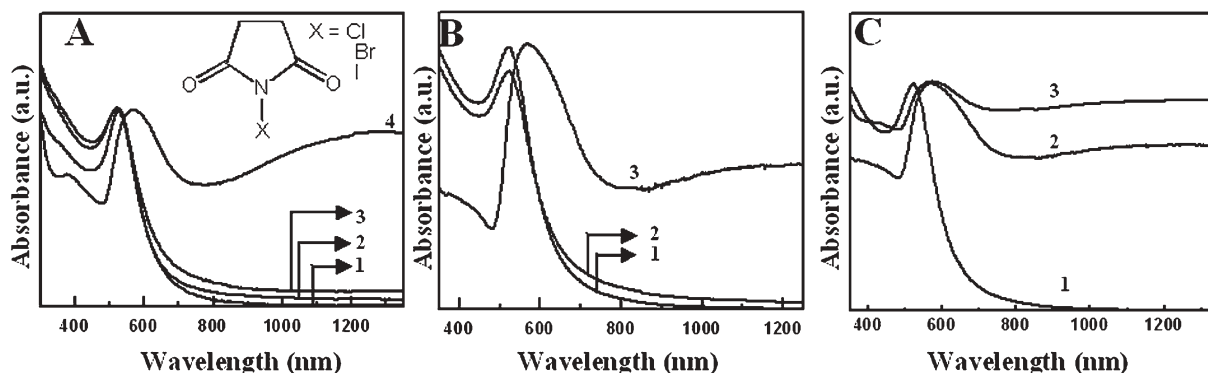
UV irradiation experiments were performed by exposing the ice-water cooled solutions of CuI added ODA nanoparticles to the UV light generated by a 450 W Hanovia medium-pressure lamp fitted with a Pyrex filter (>280 nm) for 1–2 minutes.

TEM samples for hydrophobised Au NPs, and Au NPs treated with CuI, CuBr, KI, NCS, NBS, and NIS were prepared by drop coating a few drops of resultant reaction mixtures on carbon coated copper grids and allowing them to dry. TEM measurements were performed on a JEOL model 1200EX instrument operated at an accelerating voltage of 80 kV. High-resolution TEM (HRTEM) measurements of these nanoparticles were also carried out on the same carbon coated copper grids on a JEOL-JEM-2010 UHR instrument operated at a lattice image resolution of 0.14 nm.

X-Ray diffraction (XRD) measurements of drop coated films of hydrophobised Au NPs and these Au NPs treated with CuI, CuBr, KI, NBS, NCS and NIS cast on glass slides were carried out on a Philips PW 1830 instrument operated at voltage of 40 kV and a current of 30 mA with Cu Kα radiation.

Results and discussion

Fig. 1 displays the UV-Vis spectra of octadecylamine (ODA) capped nanoparticles before and after the addition of different reagents used in this study. Fig. 1A displays the differences brought about by the addition of 1×10^{-4} M solutions of *N*-chlorosuccinimide (curve 2), *N*-bromosuccinimide (curve 3) and *N*-iodosuccinimide (curve 4) while Fig. 1B displays the changes in optical spectra after addition of 1×10^{-6} M Br$_2$

This journal is © The Royal Society of Chemistry 2007

*J. Mater. Chem.*, 2007, **17**, 1614–1619 | 1615

Fig. 1 A: Optical absorbance spectra of Au nanoparticle dispersions in chloroform (curve 1) along with those obtained after the addition of 1×10^{-4} M *N*-chlorosuccinimide (curve 2), 1×10^{-4} M *N*-bromosuccinimide (curve 3) and 1×10^{-4} M *N*-iodosuccinimide (curve 4). The molecular structure of NCS, NBS and NIS can be seen in the inset. B: Changes in optical spectra of Au NPs (curve 1) along with those recorded after addition of 1×10^{-6} M Br$_2$ (curve 2) and I$_2$ (curve 3). C: Changes in the optical absorbance spectra of ODA capped nanoparticles (curve 1) after the addition of chloroform dispersions of CuI (curve 2) and KI (curve 3).

(curve 2) and I$_2$ (curve 3). Fig. 1C highlights the changes in optical spectra upon CuI (curve 2) and KI addition (curve 3). For better comparison a plot of the pristine ODA capped nanoparticles is displayed in all the panels (curve 1). We do not know the exact concentrations of CuI and KI added as they are only sparingly soluble in CHCl$_3$; the details of their addition are mentioned in the Experimental section. Gold nanoparticle dispersions, as is well known, are ruby red coloured with an optical absorbance around 520 nm arising due to the resonant oscillation of induced dipoles with incident electromagnetic radiation.[1] A noteworthy feature of this absorbance is its dependence on the interparticle spacing with any aggregation that causes a reduction in the inter-particle spacing leading to a red shift in the peak position or sometimes leads to the development of a new peak around the NIR region apart from the peak around 520 nm.[2] Thus our spectra clearly reveal that whenever iodine is present in the reagent added the peaks are red-shifted and there appears a broad peak around the NIR region clearly suggesting aggregation to be occurring. Remarkably, no such aggregation seem to occur when any other *N*-halosuccinimides are added to ODA capped Au NPs.

To understand this feature better and to find out the real species responsible for the aggregation we repeated the experiment with molecular iodine (curve 3, panel C) as well as varied the concentration of NIS from the initial 10^{-4} M (Fig. S1, ESI†). From these we could determine that a concentration of 1×10^{-6} M iodine or 1×10^{-5} M NIS is sufficient to cause aggregation. It is also very clear that the optical spectra reveal no deviations in the peak positions when NBS/NCS or Br$_2$ are added in the same concentration regime as with NIS or I$_2$ respectively, strongly suggesting that no aggregation is occurring with their addition under these concentration conditions even after extended periods of time. Bromine forms very intense red coloured solutions at concentrations higher than 1×10^{-6} M and thus was masking the changes occurring to Au NPs precluding the study of Br$_2$ addition at higher concentrations. It should be noted that though a Br$_2$ concentration of 1×10^{-6} M is unable to bring about any change in the optical spectra, addition of I$_2$ of

similar concentration was sufficient to cause changes in the spectral features of ODA capped Au NPs.

TEM images of nanoparticles obtained after the addition of different reagents described above are displayed in Fig. 2. Fig. 2A displays the borohydride reduced nanoparticles that are capped with ODA and phase transferred into chloroform. The average size of the nanoparticles is $\sim$10 nm and they are well separated from each other forming nice hexagonally close
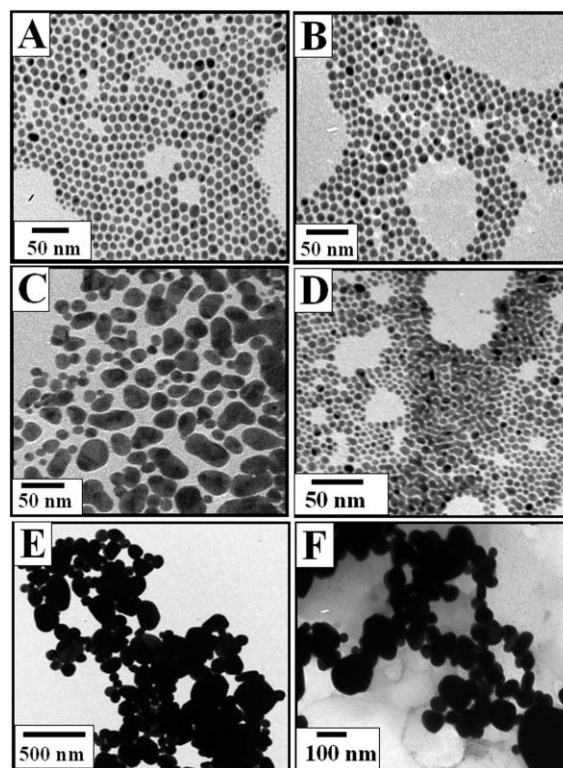
Fig. 2 TEM images of A) ODA capped gold nanoparticles; B) ODA capped Au NPs after addition of 1×10^{-4} M NCS; C) ODA capped Au NPs after addition of 1×10^{-4} M NBS; D) ODA capped Au NPs after addition of 1×10^{-6} M Br$_2$; E) ODA capped Au NPs after the addition of 1×10^{-4} M NIS and F) ODA capped Au NPs after the addition of 1×10^{-6} M I$_2$.

packed structures. In Fig. 2B the TEM image of the same nanoparticles after the addition of 1×10^{-4} M NCS is displayed. No clearly discernable changes are seen either in the optical spectra (curve 2, Fig. 1A) or the average size of the Au NPs just by NCS addition. Fig. 2C and D display the TEM images of Au NPs after they are treated with NBS and Br_2, respectively. Here it is explicitly seen that the particle morphology undergoes drastic changes with several of them losing their spherical shape and even some small aggregated/ elongated structures can be seen. However, most of the structures seen are below 30 nm and it is known that the optical properties of Au NPs below 30 nm do not differ much from their 10 nm counterparts.[1c] This probably explains why we do not see any perceivable change in the optical spectra of Au NPs treated with NBS and Br_2. The TEM images also clearly illustrate that the nanoparticles are well separated from each other. The most dramatic changes in the optical spectra are seen when Au NPs are treated with NIS or I_2 (curve 4, Fig. 1A and curve 3, Fig. 1B respectively, and curves 2 and 3, Fig. 1C). Here the TEM images related to the NIS, I_2, CuI and KI addition clearly reveal that the nanoparticles not only lose their shape but also form large aggregates (Fig. 2E and F). The TEM images, in conjunction with the optical spectra, clearly imply that these aggregates are formed in the solution itself and are not formed on the TEM grid.

There are several detailed accounts of the effect of halide ion addition to Au NPs in aqueous media.[11] The general precursor used for the synthesis of Au NPs dispersed in aqueous media is $HAuCl_4$ and it is believed that the resulting nanoparticles from this precursor would normally have adsorbed Cl^- ions released from the precursor itself. The Br^- and I^- ions are then added post synthesis and their effects on the particle morphology are investigated. Among these Cl^- ions seem to have a better alignment with the underlying Au (111) planes causing little strain.[13] On the other hand both Br^- and I^- ions also chemisorb on the gold surface with, in fact, the Au–X binding strength varying as I > Br > Cl.[14] Among the former two the I^- ion adsorption causes the greatest strain because of the largest mismatch with the Au (111) lattice plane. As mentioned above all these summaries were drawn from the study of halide addition to Au NPs formed in aqueous media. In our studies the nanoparticles are dispersed in organic media and are capped by ODA molecules. It is in general perceived that salt addition to these monolayer protected nanoparticles does not cause any change. However, our studies, which are probably the first of their kind as far as we are aware, clearly show that addition of Br_2, I_2, NBS and NIS to the organically dispersed nanoparticles also lead to changes in the shape of nanoparticles and in the case of I_2 and NIS addition result in aggregation. I_2, NIS, Br_2 and NBS probably generate small quantities of atomic species in nonpolar organic media and probably these are the species responsible for the aggregation feature observed. It has been shown earlier that free radical species could strip off the long chain organic molecules capping the nanoparticles causing their aggregation[15] strongly favouring the hypothesis that atomic species of iodine and bromine could be replacing the octadecylamine molecule capping the nanoparticle surface. FTIR spectra (ESI,† Fig. S2) recorded after the addition of NCS, NBS and NIS

to Au NPs compared with those of the virgin compounds clearly display peaks corresponding to both ODA and the succinimide part demonstrating that ODA is being replaced by these molecules on the surface. Thus, chlorine and bromine species also perhaps partially replace the surface bound ODA molecules and form an ionic adlayer on the surface by oxidizing the surface. But the charged ions probably still interact electrostatically with the replaced ODA molecules or the succinimide molecules. These organic molecules would then form a monolayer on the surface of the nanoparticles, preventing them from aggregating. However, the Br^- adsorption does create significant strain on the nanoparticle surface leading to the deformation of the nanoparticles and in some places aggregation. Iodine addition takes this story one step further. Among the three halide ions tested I^- ions form the strongest bonds with Au.[14] Then, iodine addition probably leads to the formation of a surface of AuI,[11e] which again is lattice mismatched with Au (111) planes leading to the deformation of the particles. Support for this contention comes from the XRD of Au NPs treated with iodide ions. Fig. 3 displays the XRD of ODA capped nanoparticles and NIS treated ones. It can be clearly seen that in the pristine ODA capped nanoparticles only peaks corresponding Au fcc structure are seen. However, in the NIS treated ones peaks from both Au (▲) and AuI (*) are seen clearly indicating the formation of an AuI phase most probably on the surface of the nanoparticles.[16] Then, with formation of AuI there is very little or no charge available on the surface and the ODA or succinimide molecules are no longer strongly attached to the surface leading to the aggregation of nanoparticles as observed here. It is to be noted that no peaks of AuCl or AuBr could be observed in the powder X-ray diffractograms on addition of NCS and NBS (Fig. S3, ESI†).

The next interesting part of our study is that even addition of inorganic salts like KI and CuI could result in the aggregation, similar to NIS addition. Among these the addition of KI leads to very similar results as observed for the addition of NIS with the optical spectra developing a NIR absorbance and TEM showing aggregates (Fig. 1C, curve 3 and Fig. 4A respectively). CuI addition also shows very similar transformations in the optical spectra as with KI addition
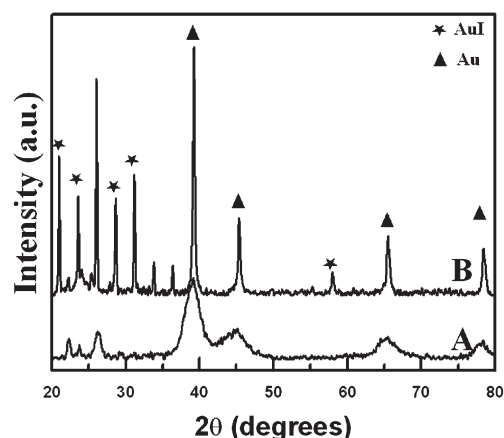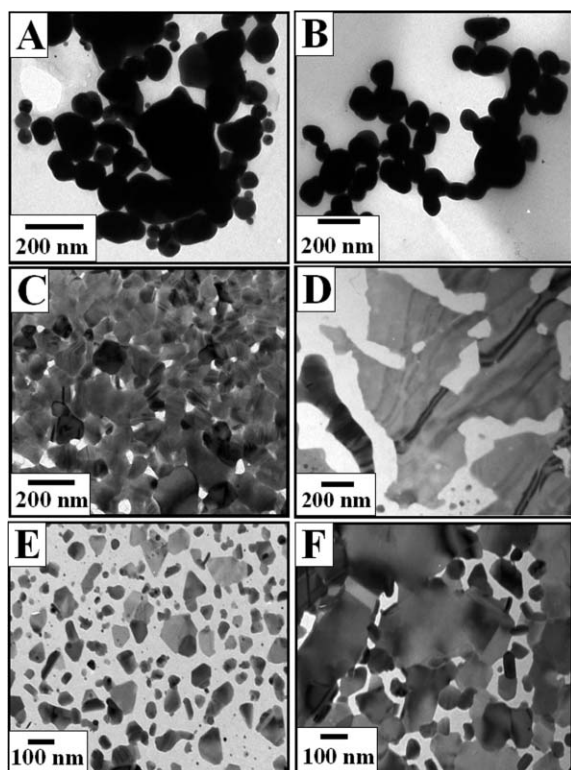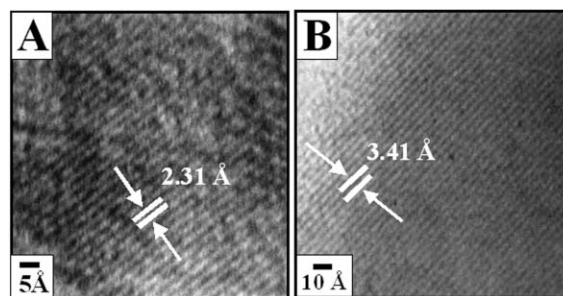

Fig. 3 Powder X-ray diffractograms of A) ODA capped gold nanoparticles and B) ODA capped Au NPs after NIS addition.

indicating aggregation (Fig. 1C, curve 2) and again in both these cases sonication of CuI and KI in CHCl$_3$ could be generating small amounts of ionic/atomic species and follow the same processes discussed above for the addition of NIS and I$_2$ addition. However, very interestingly, when a TEM grid made from the solution after addition of CuI to ODA capped Au nanoparticles is exposed to the electron beam we see some dramatic changes. There were few regions where we could see aggregates on the TEM grid and one of those which we could quickly image is displayed in Fig. 4B. Conversely, at many places we see these aggregates readily converting to flat structures (Fig. 4C and D). Similarly, when the CuI added solution was exposed to UV light we found that the structures are already formed on the grid suggesting that even UV irradiation could bring out the flattening of the structures (Fig. 4E and F).

In order to probe the nature of these flat structures we investigated them with a high resolution transmission electron microscope (HRTEM). The HRTEM images of these flat structures obtained from different locations of the grids after CuI addition and electron beam exposure are provided in Fig. 5. It can be clearly seen that the flat structures obtained are highly crystalline. The distances measured from the lattice planes on average correspond to ~2.31 Å and 3.41 Å corresponding to the lattice spacings of Au (111) planes and AuI (004) planes respectively.[13] EDS (results not shown here)

Fig. 5 HRTEM images of the flat structures obtained by the exposure of ODA capped gold nanoparticles to the e-beam after CuI addition showing the lattice spacings of A) Au(111) and B) AuI (004).

measurements also supported the presence of both Au and I. Thus it becomes very clear that the flat structures are a combination of Au and AuI, though we are not able to clearly point out which regions are rich in what composition. A point to note here is that this transformation under the electron microscope or UV irradiation occurs only with the addition of CuI (Fig. S4 and S5 in ESI†), while NIS addition and KI addition do not lead to similar phenomenon. We feel that the presence of Cu ions along with iodide ions plays a very important role in this feature. Copper, as is well known, is generally added to gold while making jewelry or structures to make it hard. Probably in this case also the presence of Cu facilitates such alloy formation decreasing the melting point in the process and leads to such flattening due to the intense heating effects of the electron beam or UV irradiation. It has been reported that electronic effects such as secondary electron generation upon exposure of monolayer protected nanoparticles to the electron beam could be very important for the coalescence of the particles.[17] The formation of alloys could facilitate such processes and hence lead to the features observed here. However we hasten to add here that these require much detailed studies and such studies are under way currently. Our efforts to probe the presence of Cu in the flat structures could not lead to any conclusive evidence due to the interference of the Cu from the TEM grid. Efforts are currently under way to study the same transformations in a grid devoid of Cu and also other studies like XPS, so that the importance of Cu in making these flat structures could be conclusively shown. It would be also interesting to study what dosage of UV irradiation or electron beam would initiate the flattening and experiments are currently under way to probe those matters in detail.

Conclusions

It has been clearly shown that addition of NBS, NIS, Br$_2$, and I$_2$ brings distinct changes to the size and shape of even monolayer protected nanoparticles. It is suggested that addition of these reagents to ODA capped Au NPs in nonpolar organic media leads to the generation of atomic species which strip off the octadecylamine capping agent, especially in the cases of bromine and iodine containing reagents. It is then proposed that these atomic species get adsorbed on the nanoparticle surfaces probably forming ionic species by oxidizing the surface. The ensuing lattice strain as a

Fig. 4 TEM images of ODA capped gold nanoparticles after A) KI addition and B–F) after CuI addition. The conversion to flat structures as observed in C and D occurs under the electron beam while the flat structures of E and F are formed in solution upon UV irradiation (see text for details) and were already present on the TEM grid before electron beam exposure.

result of the halide ion adsorption on the Au(111) planes results in morphological changes of the nanoparticle shapes. In the case of iodine the formation of AuI on the surfaces results in the maximum changes with both the shape and size being altered, and also leads to the formation of aggregates. In one interesting observation the aggregates formed by the addition of CuI to ODA capped Au NPs have been found to convert to flat structures upon electron beam exposure in the electron microscope.

Acknowledgements

References

1 (a) U. Kreibig and M. Volmer, *Optical properties of metal clusters*, Springer Verlag, Berlin, 1996; (b) S. Link and M. El-Sayed, *Annu. Rev. Phys. Chem.*, 2003, **54**, 331; (c) P. Mulvaney, *Langmuir*, 1996, **12**, 788; (d) A. Henglein, *J. Phys. Chem.*, 1993, **97**, 5457.

2 (a) K. L. Kelly, E. Coronado, L. I. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668; (b) L. M. Liz-Marzan, *Langmuir*, 2006, **22**, 32; (c) J. J. Storhoff, A. A. Lazarides, R. C. Mucic, C. A. Mirkin, R. L. Letsinger and G. C. Schatz, *J. Am. Chem. Soc.*, 2000, **122**, 4640.

3 (a) D. P. O'Neal, L. R. Hirsch, N. J. Halas, J. D. Payne and J. L. West, *Cancer Lett.*, 2004, **209**, 171; (b) L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, B. Rivera, R. E. Price, J. D. Hazle, N. J. Halas and J. L. West, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 13549; (c) X. Huang, I. H. El-Sayed, W. Qian and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2006, **128**, 2115; (d) L. A. Bauer, N. S. Birenbaum and G. J. Meyer, *J. Mater. Chem.*, 2004, **14**, 517.

4 (a) X. Xu, M. Stevens and M. B. Cortie, *Chem. Mater.*, 2004, **16**, 2259; (b) S. S. Shankar, A. Rai, A. Ahmad and M. Sastry, *Chem. Mater.*, 2005, **17**, 566.

5 (a) L. M. Liz-Marzan, *J. Mater. Chem.*, 2006, **16**, 3891; (b) S. E. Hunyadi and C. J. Murphy, *J. Mater. Chem.*, 2006, **16**, 3929; (c) M. Grzelczak, J. Pérez-Juste, B. Rodríguez-González and L. M. Liz-Marzán, *J. Mater. Chem.*, 2006, **16**, 3946.

6 R. Shenhar and V. Rotello, *Acc. Chem. Res.*, 2003, **36**, 549.

7 (a) L. Qu, G. Shi, X. Wu and B. Fan, *Adv. Mater.*, 2004, **16**, 1200; (b) T. O. Hutchinson, Y. P. Liu, C. Kiely and M. Brust, *Adv. Mater.*, 2001, **13**, 1800.

8 (a) B. V. Derjaguin and L. Landau, *Acta Physicochim. URSS*, 1941, **14**, 633; (b) E. J. Verwey and J. T. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.

9 (a) B. A. Korgel, S. Fullam, S. Connolly and D. Fitzmaurice, *J. Phys. Chem. B*, 1998, **102**, 8379; (b) P. J. Thomas, G. U. Kulkarni and C. N. R. Rao, *J. Phys. Chem. B*, 2000, **104**, 8138.

10 (a) I. Hussain, Z. Wang, A. I. Cooper and M. Brust, *Langmuir*, 2006, **22**, 2938; (b) D. S. Sidhaye, S. Kasyap, M. Sastry, S. Hotha and B. L. V. Prasad, *Langmuir*, 2005, **21**, 7979; (c) S. Tamang, S. Hotha and B. L. V. Prasad, *J. Nanosci. Nanotechnol.*, in press.

11 (a) A. Rai, A. Singh, A. Ahmad and M. Sastry, *Langmuir*, 2006, **22**, 736; (b) S. S. Shankar, Ph. D. Thesis, University of Pune, 2006; (c) L. Linaert, P. Mulvaney and A. Henglein, *J. Phys. Chem.*, 1993, **97**, 679; (d) S. Pang, T. Kondo and T. Kawai, *Chem. Mater.*, 2005, **17**, 3636; (e) W. Cheng, S. Dong and E. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 449; (f) T. Pal, N. R. Jana and T. K. Sau, *Corros. Sci.*, 1997, **39**, 981.

12 (a) A. Filankembo and M. P. Pileni, *J. Phys. Chem. B*, 2000, **104**, 5865; (b) A. Filankembo, S. Giorgio, I. Lisiecki and M. P. Pileni, *J. Phys. Chem. B*, 2003, **107**, 7492.

13 (a) P. Gao and M. J. Weaver, *J. Phys. Chem.*, 1986, **90**, 4057; (b) O. M. Magnussen, B. M. Ocko, R. R. Adzic and J. X. Wang, *Phys. Rev. B: Condens. Matter*, 1995, **51**, 5510.

14 (a) O. M. Magnussen, B. M. Ocko, J. X. Wang and R. R. Adzic, *J. Phys. Chem.*, 1996, **100**, 5500; (b) B. M. Ocko, G. M. Watson and J. Wang, *J. Phys. Chem.*, 1994, **98**, 897; (c) S. A. Wasileski and M. J. Weaver, *J. Phys. Chem. B*, 2002, **106**, 4782.

15 A. J. Kell, A. Alizadeh, L. Yang and M. S. Workentin, *Langmuir*, 2005, **21**, 9741.

16 The XRD patterns were indexed with reference to the crystal structures from the ASTM charts: AuI (chart card no.15-0521) and Au (chart card no. 04-0784).

17 Y. Chen, R. E. Palmer and J. P. Wilcoxon, *Langmuir*, 2006, **22**, 2851.