UV-Vis plasmon studies of metal nanoparticles

J W L Eccles\textsuperscript{1}, U Bangert\textsuperscript{1}, M Bromfield\textsuperscript{2}, P Christian\textsuperscript{2}, A J Harvey\textsuperscript{1}, P Thomas\textsuperscript{3}

\textsuperscript{1}Materials Science Centre, The University of Manchester, Grosvenor Street, Manchester, M1 7HS, UK
\textsuperscript{2}School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK
\textsuperscript{3}Gatan UK, 25 Nuffield Way, Abingdon, OX14 1RL, UK

James.Eccles@postgrad.manchester.ac.uk

Abstract. Previous studies of the surface plasmon resonance (SPR) from alloy nanoparticles of gold and silver have focused on bulk studies of the nanoparticles in solution. Here, we present a selection of data observed from individual alloy nanoparticles using highly spatially resolved electron energy-loss spectroscopy (EELS). In order to resolve the SPR in both the pure gold and Au-Ag alloy nanoparticles, we successfully applied the Richardson-Lucy deconvolution routine. We found that resonances observed from different sized alloy nanoparticles do not follow the same trends in frequency variation as their pure metal equivalent. Additionally, we do not consistently observe a single SPR peak, as one might expect from an alloy nanoparticle. This indicates that alloy nanoparticles, produced by the simultaneous reduction of metal salts, cannot be considered truly homogeneous.

1. Introduction

Surface plasmons are created on the boundary of a metal. These represent quantised oscillations of surface charge produced by an external electric field [1]. The SPR excited on metal nanoparticles creates interesting optical properties. In solution, gold nanoparticles appear red in colour, whilst silver nanoparticles appear yellow. This is caused by the differing frequency of the SPRs in the two metals. For surface plasmons on metal nanoparticles there are a number of resonance modes (\( \ell \)). The most important of these is the \( \ell = 1 \) resonance (Mie mode) which has an optically active dipole field configuration [2]. For nanoparticles of gold, silver and copper, this dipole resonance occurs in the UV-Vis region making the nanoparticles useful for optical applications [3][4]. As well as the dielectric properties of the material, the frequency of the dipole resonance depends upon the size and shape of

![Figure 1. HR-TEM image of Au-Ag alloy nanoparticles on a lacy carbon film substrate.](image-url)
nanoparticles [5]. This enables nanoparticles to be ‘tuned’ to different frequencies by varying these properties. For spherical nanoparticles, the greatest frequency range can be achieved by alloying the metals of gold and silver at different relative concentrations. These resonances can be scrutinised in bulk solution using UV-Vis Spectroscopy [6]. However, these resonances are a result of the superposition of resonances from individual nanoparticles, which may have a range of frequencies due to variations in size. Using a field emission gun (FEG) scanning transmission electron microscope (STEM) system, and the EELS technique, we have been able to observe the resonances of individual nanoparticles with a high degree of spatial resolution.

2. Methodology

The alloy nanoparticles were produced using equal molar amounts of the metal salts, silver nitrate and gold chloride. These salts are added to a solution of sodium citrate [7]. Sodium borohydride (SBH) is then used to reduce the metal ions to the metal. The use of sodium borohydride is advantageous since the reaction is rapid and the solution does not require heating. The citrate particles do not contribute to this reduction, but rather act as a stabiliser for the particles. The resulting nanoparticles were deposited on to a lacy carbon film substrate for analysis. Initial examination of the nanoparticles using high resolution transmission electron microscopy (HRTEM) analysis was carried out using a Tecnai F30 TEM operating at 300 kV. This revealed the nanoparticles ranged in size from ~ 3 nm up to 30 nm in diameter. Figure 1 represents a HRTEM image of several of the smaller-sized particles. The EEL spectra were acquired using a VG HB-601 STEM operated at 100 keV and equipped with a Gatan Enfina spectrometer. The STEM provides an energy resolution of 0.35 eV and is capable of a high dispersion (0.01 eV per channel). These factors enable the partial resolution of features close to the high energy zero loss peak ZLP tail. An objective aperture semiangle of 21.3 mrad was applied to limit the effect of spherical aberration, and to provide good imaging conditions. A collector aperture semiangle of 1.34 mrad was used to prevent saturation of the detector.

The FEG, with an achievable energy resolution of around 0.35eV, has in the past enabled the direct observation of the SPR in silver nanoparticles at around 3eV. However, for nanoparticles of gold and the Au-Ag alloy, the SPR in both cases, is obscured by the high energy tail of the ZLP. We therefore applied the Richardson-Lucy (R-L) deconvolution algorithm to ‘improve’ the energy resolution of the spectra and to enable the SPR frequency to be observed. The RL deconvolution algorithm [8][9], whilst not necessarily being an alternative to monochromation, has been shown to be effective at improving the energy resolution of both valence-band and core-loss spectra [10][11]. It has also been successfully applied to silver nanoprisms in order to map the SPR [12]. The method assumes that the degraded image H is of the form;

\[
\text{Figure 2. Deconvolved EEL spectrum from a gold nanoparticle (12nm diameter) up to 4 iterations. The surface plasmon is detectable a 2.4 eV.}
\]
where \( W \) is the original image and \( S \) is the point spread function (PSF). The algorithm estimates the original image by deconvolving the degraded image with a PSF. The advantage of this routine is that it is able to conserve the total spectrum intensity and as such can cope with EEL spectra with a high dynamic range, such as the intense ZLP and weak plasmon features. The main disadvantage is that for statistically noisy data strong noise amplification arises. However, since the algorithm is iterative, it is possible to cease the process before any noise components are significantly amplified. As will be demonstrated, the use of 3-4 iterations is successful in resolving the required features without any artefacts being introduced. Figure 2 shows the R-L deconvolution routine applied to low loss spectra obtained from the surface of a gold nanoparticle. Following deconvolution up to 4 iterations, the SPR can be observed at 2.4 eV.

3. Results and Discussion

Initial studies were conducted to examine SPR behaviour in pure gold and silver nanoparticles. EEL spectra were obtained for individual nanoparticles by summing multiple spectra from the surface edge of each particle, as indicated in Figure 2 (----). Figure 3 (a) shows the variation in energy loss (frequency) as the size of the nanoparticles is varied. For silver particles with a diameter greater than 15 nm, the SPR frequency is governed largely by the dimension of the particle with respect to the

![Figure 3](image_url)

**Figure 3** (a). Surface plasmon excitation energies for pure gold and pure silver nanoparticles of different particle diameter. Both pure gold and silver nanoparticles have a single SPR in the low energy regime. Silver nanoparticles have an additional bulk resonance at 3.8 eV, which only becomes dominant for larger sized particles. (b) EEL spectra from Au-Ag alloy nanoparticles deconvolved up to 3 iterations where arrows indicate a resolvable second resonance. The spectra are displaced vertically to make the comparison easier.
wavelength of the incoming radiation. This relationship results in a red shift in SPR frequency. For silver nanoparticles within this size regime we consider the dielectric function to be constant as a function of the radius of the particle $\varepsilon(\omega)$. However, as the size of the particle decreases, the relative size and importance of the surface layer increases. For silver nanoparticles with a diameter $< 15$ nm, the effective surface layer can no longer be considered a constant and the dielectric function of the material varies as a function of particle size $\varepsilon(\omega,r)$ [13]. This is known as the quantum size effect, and is a well documented nanoparticle behavior [14]. As the particle size is reduced, the quasi-continuous band structure begins to separate into discrete energy levels. This causes a blue-shift in plasmon energies. This size associated red and blue frequency shift is also observed for the gold nanoparticles, however this shift occurs at different energies due to the differing dielectric properties.

Figure 3 (b) shows the EEL spectra acquired from single Au-Ag Alloy nanoparticles deconvolved up to 3 iterations. At this level of deconvolution, the SPR can clearly be identified. One would expect, as in the case of the pure metal particles, to observe a relative shift in the nanoparticles towards a greater energy loss as particle diameter is decreased. However, this is not the case, as the energy loss of the SPRs appears to be random and show no specific trend. This could indicate the effect of other influencing factors on the energy loss of the SPR, such as the dielectric properties of the material. This suggests the dielectric function could differ from particle to particle, due to in homogeneity in the alloy. Additionally, we observe a distinct broadening of the SPR in the case of the 7.7 nm particle, and a small higher energy secondary peak indicated for 7.2 nm and 10 nm particles. This could represent segregation of the two metals within the nanoparticle. Specifically, a concentration of silver on the surface of the nanoparticle could be responsible for this second feature.

4. Conclusion
In conclusion we show that the nanoparticles cannot be considered truly a homogeneous alloy. Unlike the quantum size effects displayed by the pure metal nanoparticles, the random behaviour of alloy SPR must indicate variations in the dielectric function of each particle. It is possible this is caused by different relative concentrations of silver and gold within the particle. There is also evidence of segregation within the particles, particularly owing to excitation of a weak resonance at energies associated with pure silver SPR excitations. This indicates a possible core/shell type structure, with a thin outer shell of silver. This would support UV-Vis investigations where specifically produced core/shell particles display a twin peak structure in the extinction spectra [15].

References

[1] Raether H 1977 New York Surface Plasma Oscillations and Their Applications. In: Physics of Thin Films Vol. 9 145-171
[2] Mie G 1908 Ann. Phys. 25 377
[3] Xu H, Bjerneld EJ, Kall M and Borjesson L 1999 Phys. Rev. Lett. 83 4357-4360
[4] Ebbesen TW, Lezec HJ, Ghaemi HF, Thio T and Wolff PA 1998 Nature 391 667
[5] Lance Kelly K, Coronado E, Zhao T and Schatz GC 2003 J. Phys. Chem. B 107 668-677
[6] Papavassiliou GC 1976 J Phys. F: Metal Phys. 6 103-105
[7] Henglein A and Giersig M 1999 J. Phys. Chem. B 103 9533-9539
[8] Richardson WH 1972 J. Opt. Soc. Am 62 55
[9] Lucy LB 1974 Astro. Journal 79 745-754
[10] Goter A, Douiri A, Tencé M and Colliex C 2003 Ultramicroscopy 96 385-400
[11] Kimoto K, Ishizuka K, Mizoguchi T, Tanaka I and Matsui Y 2003 J. Elec. Micro. 53 299-303
[12] Nelayah J et al 2007 Nature Physics. 3 348 - 353
[13] Kreibig U and Vollmer M 1995 Berlin Optical Properties of Metal Clusters 13-21
[14] Ouyang F, Batson PE and Isaacson M 1992 Phys. Rev. B 46 15421-15425
[15] Morriss RH and Collins LF 1964 J. Chem. Phys. 41 3357-3363