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Emilie Ringe[1] **, Richard P. Van Duyne**[2]**, Laurence D. Marks**[3]

[1] Department of Materials Science and Metallurgy, Cambridge University, 27 Charles Babbage Road, Cambridge CB3 0FS, UK
[2] Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA
[3] Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, IL 60208, USA

Abstract. Interest in nanotechnology is driven by unprecedented means to tailor the physical behaviour via structure and composition. Unlike bulk materials, minute changes in size and shape can affect the optical properties of nanoparticles. Characterization, understanding, and prediction of such structure-function relationships is crucial to the development of novel applications such as plasmonic sensors, devices, and drug delivery systems. Such knowledge has been recently vastly expanded through systematic, high throughput correlated measurements, where the localized surface plasmon resonance (LSPR) is probed optically and the particle shape investigated with electron microscopy. This paper will address some of the recent experimental advances in single particle studies that provide new insight not only on the effects of size, composition, and shape on plasmonic properties but also their interrelation. Plasmon resonance frequency and decay, substrate effects, size, shape, and composition will be explored for a variety of plasmonic systems.

1. Introduction

Gold and silver nanoparticles are the object of intense research because of their fascinating nanoscale behavior. These metals display bright colors when particles of sizes of a few to a few hundreds of nanometers are dispersed in a medium or on a surface. A striking example of this is the yellow and red in medieval stained glass, typically resulting from the incorporation of small silver and gold particles, respectively. The phenomenon responsible for such optical behavior is a localized surface plasmon resonance (LSPR), a coherent oscillation of the electrons in a particle generally smaller than the wavelength of light. This resonance can occur in a variety of materials, however, the ease of fabrication and shape control, stability, well-known surface chemistry, and biocompatibility give Au and Ag a prominent place in the burgeoning field of plasmonics.

The applications of plasmonically active nanoparticles stem from the three wavelength-dependent effects of LSPR: photon absorption, elastic photon scattering, and local enhancement of the electric field at the surface of the nanoparticle. The latter is responsible for the majority of the signal enhancement observed in surface enhanced spectroscopies such as surface-enhanced Raman, fluorescence, and second harmonic generation [1-4]. Photon scattering is most prominent in larger particles and is important in practical sensor implementation and imaging contrast agents [5,6]. Finally, photon absorption leads to plasmon excitation, which subsequently decays through a variety of mechanisms, amongst which many ultimately raise the temperature of the nanoparticle surface, leading to localized heating that can be harnessed to boil liquids or destroy cancerous tissues [7,8].

The above examples are not an extensive list, but they highlight the breadth of applications potentially realizable with plasmonics, given sufficient knowledge and understanding of the underlying resonance phenomenon.

Size, shape, composition, and the surrounding environment provide multiple handles to tune the electron oscillation behavior; the latter being the basis of a number of refractive index sensors [9-11]. It is well known that each of those factors strongly affects the plasmon energy, decay, near-field distribution, and refractive index sensitivity. Mie theory, even in its simplest form (the electrostatic approximation), predicts the importance of shape, composition, and surrounding environment [12]. Many studies have aimed at unraveling the effects of such factors for non-spherical shapes, providing some general rules. However, in the vast majority of these approaches, the many relevant structural (shape, size, composition) and environmental (substrate, surrounding medium) factors have been investigated independently, despite the lack of evidence for their independence. Synthetic limitations, insufficient data size and range, as well as correlation difficulties have hindered progress in understanding such multi-component problems.

In this paper, we discuss the techniques we have developed to surmount many difficulties related to single particle analysis, and present a survey of our recent results on the effects uniquely probed via single particle experiments as well as the interrelation of structural and/or environmental factors on the plasmonic behavior of gold and silver nanoparticles.

2. Methods and methods development

Advances in shape control have led to vast improvements in the yield of anisotropic nanoparticles, as well as their size distribution. However, averaging over the unavoidable shape and size in homogeneities prevents obtaining a detailed understanding of the structure-function relationships; additionally, information about polarization dependence as well as plasmon decay cannot be obtained from a bulk sample. Single particle methods provide unique opportunities to learn about how the minutest structural and environmental factors influence the optical properties of plasmonic particles.

The first correlated, single particle results are attributed to Tamaru *et al.*[13] and Mock *et al.*[14], who coupled optical dark field microscopy results with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses, respectively. Since these early studies on colloidal silver particles, many different experimental approaches have been employed to gain insight on the structure-function relationship in gold and silver nanoparticles, integrating optical absorption techniques, atomic force microscopy, etc; see for instance the recent reviews [15-17] for additional information. These provide a powerful way to observe the effects of structural parameters on optical properties, and, when used in conjunction with statistical analysis, yield predictive rules regarding the effects of size, composition, corner rounding, interparticle coupling, and surrounding environment on the plasmon energy, and lifetime.

Our studies used a combination of optical dark field microscopy and transmission electron microscopy. In dark field microscopy, the sample is illuminated with a hollow cone of white light (possibly polarized), and only the scattered light is collected, creating a dark background as shown in Fig. 1, and providing an excellent signal-to-noise ratio for the particles studied (>50 nm). TEM was chosen as the structural characterization tool because of its superior spatial resolution. We established that optical measurements must be performed prior to electron illumination, as it causes irreversible damage and/or contamination [15]. In practice the experiment is carried out as follows. Nanoparticles are deposited on TEM-compatible substrates (C/Formvar, Si_3N_4, SiO_x, etc), and excess surfactants are removed with an appropriate solvent, attempting not to change the particle morphology (which can happen). Then the spectrum of individual particles is acquired by centering the scattering signal (diffraction-limited spot) on the slit of a spectrometer/detector (CCD), integrating over the height of the spectrum on the CCD. An optical image covering a large sample area is used to number the particles and subsequently serves as a map to retrieve the region of interest once the grid is inserted in a TEM. The entire process allows for the collection of hundreds of correlated single particle data per sample. Obtaining such large data sets is critically important as they enable statistical analysis with relatively small errors, and allow multi-dimensional investigations.
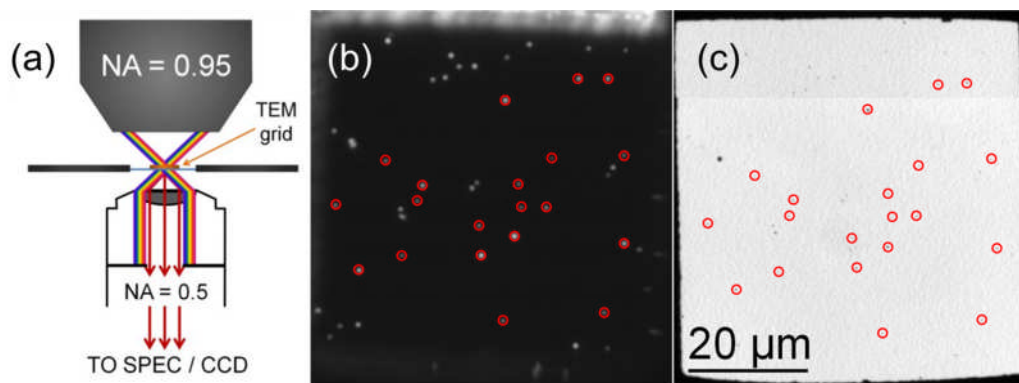
Figure 1. Setup for correlated DFM/TEM measurements. (a) DFM geometry. (b) Black and white optical image used as map for numbering and retrieving single diffraction-limited spots. (c) TEM image of the corresponding area. Reproduced with permission from ref [18].

3. Experimental results: new insight from statistical analysis of single particle data
3.1. Interrelation of size, composition, and dielectric environment on nanocubes

Owing to their high symmetry and flat faces rendering them stackable, and the high electric field enhancement at their sharp corners, plasmonic nanocubes are interesting structures for applications involving device fabrication. Many factors influence their LSPR energy, and to fully investigate and quantify such factors we studied Ag and Au nanocubes of sizes 60-100 nm on two representative substrates: a polymer (Formvar, refractive index n=1.5) and a semiconductor, (Si_3N_4, n~2)[19]. Several effects and interrelations were obtained from analysis of covariance of the data obtained on 175 individual nanocubes (figure 2)[19]. Note that the LSPR FWHM for particles on Si_3N_4 (n~2) could not be determined with acceptable error levels due to etaloning and noise, most pronounced in the blue region (affecting Ag cubes most), hence are not reported.
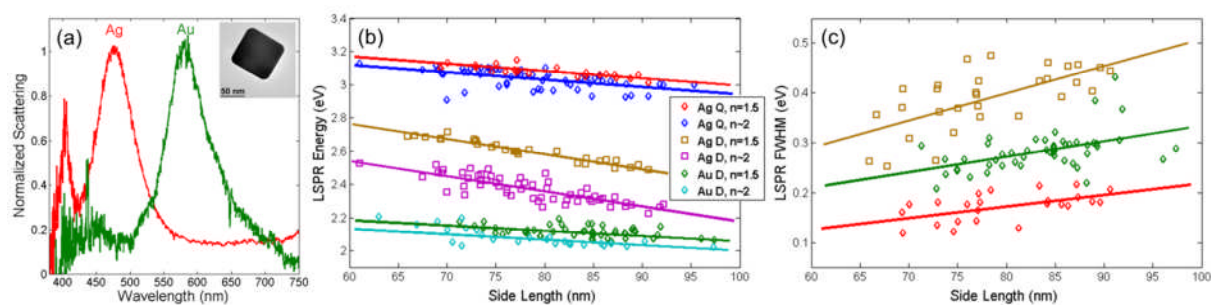

Figure 2. Correlated LSPR/TEM measurements on nanocubes. (a) typical LSPR spectra showing the sharp quadrupole-like resonance in Ag nanocubes, as well as the broader dipole-like resonance in both Ag and Au particles. Interrelation of composition, dielectric environment, and size on the (b) plasmon resonance energy and (c) plasmon FWHM for gold and silver nanocubes on Formvar (n=1.5) and Si_3N_4 (n~2) substrates. The legend applies to both (b) and (c).

As expected from phase retardation effects and radiation damping, the LSPR energy and peak width shifts to the red and broadens with increasing size, respectively, and the LSPR energy for a given size decreases with increasing refractive index of the substrate. Also, in Ag, the quadrupole-like mode (distal) is higher in energy than the dipole-like mode (proximal) for all sizes observed. The interrelations between these factors are more interesting, however, and uniquely addressed using large sets of single particle data. From figure 2, it is immediately evident that the size dependence (the slope) of the energy and FWHM depends on the composition, and, in the case of Ag, mode symmetry, but not on the substrate, as can be proven with analysis of covariance. The LSPR energy size

dependence for the Ag dipole (-8.9(5) meV/nm, standard deviation on the last digit in parenthesis) is over twice as large as that of the Ag quadrupole (-4.2(6) meV/nm), which is in turn comparable to that of the Au dipole (-3.9(6) meV/nm). The size dependence of the FWHM also follows a similar trend, with that of the Ag dipole being highest (5.4(1.2) meV/nm), followed by the Ag quadrupole and Au dipole (3.1(8) and 2.3(7) meV/nm). Also, the magnitude of substrate effects is dependent on the mode and composition, but not particle size; the difference in LSPR positions on Formvar and Si_3N_4 are 0.23 and 0.057 eV for the dipolar modes of Ag and Au, respectively; it is 0.053 eV for the Ag quadrupolar mode. While a small change of the size-dependence (different slope in figure 2b) is expected for Au sphere in different dielectric environments [20], this effect was not observed in cubes and other shapes we investigated (decahedra, icosahedra, truncated bitetrahedra; results not shown). This is due to the small range of dielectric constants studied; the effect could only realistically be seen for changes of over a refractive index unit.

Understanding such interrelations between size, composition, and dielectric environment is essential to a holistic design of plasmonic sensors and devices. For example, in the design of a sensor, it is always best to have a narrow peak; if this sensor is based on a random particle array, the quadrupole-like mode of Ag should appeal considerably more than the other modes, as it is sharp and the size dependence of both its energy and width is low, reducing heterogeneous broadening in an ensemble. It should also be possible to interpolate the energy values between those obtained for Formvar and Si_3N_4, providing further predictive power to these finding.

3.2. Interrelation of size, shape, and corner rounding
The very first correlated shape-LSPR measurements on nanoparticles pointed out the critical importance of corner rounding on optical properties, and since then, very few studies systematically probed its effects despite the ever-present inhomogeneities in synthesized and fabricated samples. Indeed, in typical solutions of nanocubes and bipyramids, rounding can range from a few to a few tens of nm. Rounding is responsible for a significant amount of scatter in figure 2 and similar plots in the literature. In fact, corner geometry has a major impact not only on the resonance energy and width, but also on the size effects: rounded particles do not have the same size-dependence of the LSPR energy as sharp particles. This conclusion was reached from the statistical analysis of the two large data sets in figure 3, on Au cubes and Ag bipyramids. The equations describing the multiparameter fits, and their associated error (95% confidence level on the coefficients), were found to be

Bipyramid LSPR (eV) = -0.0051(3)*a(nm) + 0.019(3)*r(nm) + 2.69(6)   (1)
Cube LSPR (eV) = -0.0039(15)*a(nm) + 0.007(2)*r(nm) + 2.34(12)   (2)

Where a is the particle size (side length for cube, height of the triangular base for bipyramids), and r is the truncation and rounding as defined in [18,19]. Such well-characterized coefficients provide evidence that rounding is not simply reducing the length of a particle; by affecting the near-field distribution, rounding contributes more than the equivalent change in distance between the tips of a particle, i.e. the effect is not only geometric. Indeed, if it were the case, and truncation would simply lower the distance between poles of opposite charges in the dipolar resonance, the coefficient of r in equation 1 would be negative with a value equal to the coefficient of a), i.e. a fit relating the plasmon energy to the truncated height (a-t) would be best. Clearly, this is not the case as the rounding coefficient is, for bipyramids, about four times the size coefficient. This effect is also observed in computational results on Ag and Au rods based on Mie-Gans theory [18,21]. It is thus important to consider rounding when making predictions of the plasmon behaviour.
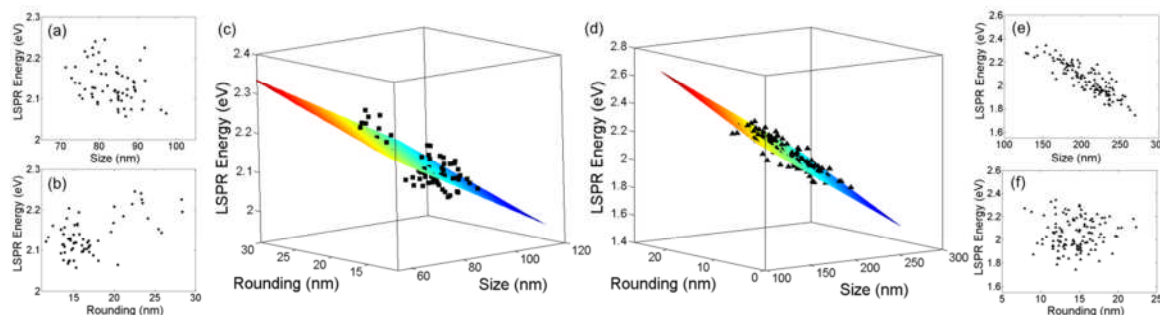
Figure 3. Multi-parameter fits of the LSPR energy dependence on size and corner rounding show similar behaviour in Au nanocubes (a-c) and Ag bipyramids (d-f). Parts d-f adapted with permission from ref.[18]

4. Outlook, opportunities and limitations

Given that structure is a powerful handle to tune the optical response of plasmonic nanoparticles, characterizing structure-function relationships is important in the fundamental understanding of the phenomenon as well as in the design of plasmon-based devices. The high-throughput techniques and statistical analysis presented here yield a more complete and quantitative understanding of such structure-function relationships. The effect of rounding, composition, substrate and size were found to be interrelated, and given the large data sets obtained, this interrelation could be explored, leading to better understanding of size and rounding, as well as quantitative, predictive rules.

Results on single particles can thus be a powerful tool to study materials; however, they are not necessarily the only choice, and clearly not always valid. In the case of small data sets with large variations in multiple components (size, shape, rounding, etc), results may be misleading or have no statistical significance; tests should always be performed on such data to confirm the significance and provide the errors associated with the quantification.

Single particle investigation and structure-function relationships need not be limited to the investigation of the plasmon energy and width correlated with particle shape. In fact, optical-structural correlations can be used to probe a variety of systems, revealing and quantifying other phenomena such as enhancement factor in surface-enhanced Raman spectroscopy[22], polarization-dependent behaviour in anisotropic nanoparticles[13], absorption[23], etc. It is expected that such correlative approaches will provide important clues on the behaviour of nanoparticles, even beyond plasmonic systems. However, introducing new instruments and/or techniques result in additional difficulties related to obtaining a sufficient amount of data to quantify the effects studied; this constraint currently affects refractive index sensitivity, elemental analysis in alloys, and polarization measurements, for example.

Most correlative measurements involve electron microscopy as a structural characterization tool; images are almost exclusively used to measure the size and shape of the nanoparticles. Electron microscopy offers a much larger range of tools, however. The interaction of the electron beam with a metal particle can be used to probe the near field behaviour of plasmon resonances, i.e. the electric field surrounding the particle as a result of electron oscillation at its surface [24]. However, the energy resolution of electron-based techniques, at best around 0.1 eV, is two orders of magnitude worse than that of optical measurements (easily few meV), and instrumentation is vastly more costly. Electron-based approaches are still tremendously useful because of their unsurpassed spatial resolution, an attribute impossible in optical spectroscopy due to the large wavelength of visible light.

Acknowledgments

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