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Blue-shifted plasmon resonance of individual size-selected gold nanoparticles

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Abstract

The future implementation of integrated photonic devices requires the creation of nanostructures with well defined morphological and optical properties. To this end, we deposited size-selected gold nanoparticles produced by a gas phase aggregation cluster source on transparent substrates at room temperature with controlled impact energy. Interferometric optical detection measurements using a supercontinuum laser source demonstrated a blue-shifted plasmon resonance at the single particle level. The blue shift was observed to be more pronounced for small single clusters down to 3 nm in size.

1. Introduction

The preparation, deposition and optical characterisation of well defined nanoparticles on suitable optical substrates are of importance for future generations of integrated photonic circuits, biosensors, and energy conversion. To this end, we are exploiting the precise and controlled preparation and deposition of small size-selected gold nanoparticles on transparent substrates [1] prepared by a gas phase aggregation cluster source [2–4]. It is well known that gold nanoparticles exhibit a local surface plasmon (LSP) resonance when excited by an electromagnetic field [5–8]. These resonances give rise to interesting optical properties and effects such as: fluorescence enhancement [9–11]; enhanced Raman scattering [12,13]; scattering, absorption and extinction which depend on the geometrical shape and environment of the nanoparticles [14–16]; second harmonic generation (SHG) and 4-wave-mixing (4WM) [17–19]; etc.

In the present work we prepared monodispersed size-selected gold particle films and optically characterised them at the single molecule level down to sizes of 3 nm. A clear plasmon resonance is detected from an individual nanoparticle using an interferometric detection setup with a supercontinuum laser source. Additionally, we observe a spectral blue shift that depends on the nanoparticle size.

2. Experimental

The size-selected gold particles were produced in a magnetron sputtering, gas phase aggregation cluster source [2,3] and mass selected with 5% resolution by a novel lateral time of flight mass filter [4]. The particles were then deposited onto a PMMA coated glass coverslip in a low density fashion. The preparation and the morphological characterisation are reported elsewhere [1].

The optical configuration was implemented following the interferometric technique reported elsewhere [20], in order to reach a single molecule detection level. A Nikon Eclipse 300 inverted microscope was used as the main optical system. A supercontinuum laser source was employed and coupled into the microscope. The schematic of the whole setup is illustrated in Fig. 1. A ~200 fs Ti:Sapphire laser (Mira) with 0.9 W average power, 76 MHz repetition rate and 800 nm as a pump wavelength was used to generate the supercontinuum light from a photonic crystal fiber

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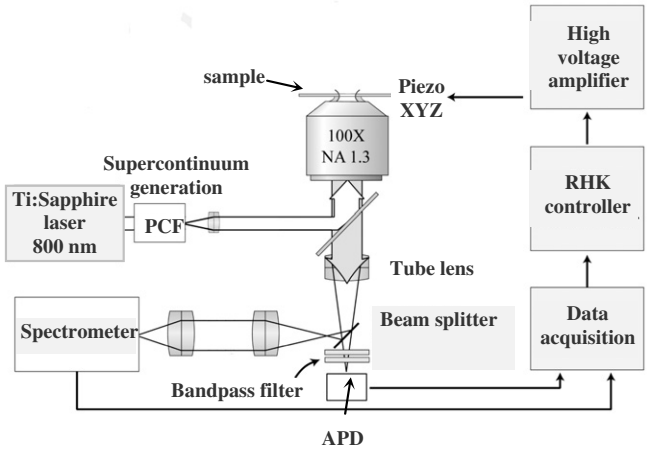

Fig. 1. Interferometric detection system for plasmon measurements at the single molecule detection level.

(PCF). The pure silica fiber (90 cm long) had a zero dispersion wavelength at 730 nm with a core of about 2 μm (ThorLabs). The coupling was done by an IR coated aspheric lens with a numerical aperture (NA) of 0.25. The light at the output of the fiber was collected and collimated before entering into the microscope in order to slightly overfill the back aperture of the objective, a Nikon 100× Plan-Fluor, with NA 1.3. The sample was mounted on a closed-loop piezoelectric driven stage in order to raster the sample typically over a range between 10 and 50 μm. An avalanche photodiode (APD) – SPCM-AQR-16 from Perkin Elmer – in a single photon counting configuration was mounted onto the front port of the microscope, in order to collect the intensity image and to have a good degree of confocal detection (active area ~170 μm^2). The side port of the microscope was coupled to a fixed grating visible spectrograph (ARC – Acton Research Corporation) equipped with a thermoelectrically cooled CCD camera (Andor). The sample was rastered until a single particle was detected in the intensity image. After acquiring the spectrum for a single particle, a second spectrum was recorded to the side of the particle providing a background reference spectrum. The two spectra were then post-processed and analysed.

3. Results and discussion

We measured the plasmon resonance spectra for Au particles deposited on a transparent substrate and compared the results with theoretical predictions. In order to avoid inhomogeneous broadening due to particle variations or local environments we performed single particle measurements.

Positively charged size-selected Au_{11080} and Au_{878} clusters were deposited on a soft PMMA coated quartz substrate at very low density. The coating was used to provide a soft-landing medium, in order to limit as much as possible the morphological change upon impact. Furthermore, the PMMA coating also smoothes down the mean roughness of the underlay supporting substrate to 0.4–0.8 nm, giving weaker optical scattering by the surface. We did not observe any cluster–polymer interaction. We believe this is small due to the absence of any chemical interaction between the deposited clusters and the polymer surface. Moreover the size-selected clusters were prepared in high vacuum from a pure gold target, and the polymer was previously baked out above its glass-transition temperature. Finally, the deposition was performed in soft-landing regime, i.e. low impact energy. The dielectric function of the surrounding matrix (immersion oil and polymer layer) was considered to be the only external parameter which influences the gold cluster plasmon resonance [21].

Fig. 2 illustrates a topographic atomic force microscopy (AFM) image of size-selected Au_{11080} clusters deposited on a PMMA coated quartz substrate prior to optical characterisation. The image shows clearly that the cluster density is low enough to allow optical measurements at the single particle level. On the PMMA surface the clusters should stay firmly immobilised at the landing site, approximately retaining their gas phase geometrical structure [1]. A small degree of cluster flattening after the impact on the surface was observed, even though the cluster deposition was performed in the low energy cluster beam deposition (LECBD) regime (impact energy less than 1 eV per atom) [1]. We measured in detail, by scanning transmission electron microscopy (STEM), the size-selected cluster structure in the range 300–30,000 atoms, after LECBD deposition on

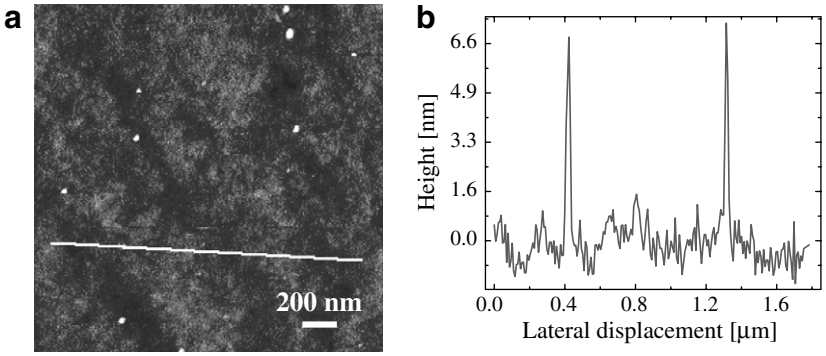

Fig. 2. (a) Shear force imaging of Au_{11080} clusters on a PMMA coated quartz prior to dropping the immersion oil onto the top surface; (b) corresponding line profile.

amorphous carbon coated TEM grids. They retain a quasi-spherical shape across the whole range [22]. A detailed analysis on Au_{309} clusters, coupled with theoretical simulations, confirmed the quasi-spherical interpretation with well defined polyhedral shapes [23].

After dropping a small amount of immersion oil on the top surface, the plasmon measurement was carried out. Fig. 3a shows the intensity image of individual nanoparticles with the corresponding line profile in Fig. 3b. After identifying a single particle, the plasmon resonance was recorded by directing the backscattered light into the spectrograph. The result for individual Au_{11080} particles is depicted in Fig. 3c, where the theoretically calculated curve is also shown for comparison. Similar experiments previously performed with monodispersed gold colloids of various sizes (80 nm, 40 nm, 20 nm) provided an experimental reference point for the analysis of the recorded data. The data collected (not reported here) showed excellent agreement with the calculated plasmon curves.

The measured plasmon peak for Au_{11080} particles is found at 535.3 nm which is different from the calculated peak position of 549.4 nm. The distinct blue shift is attributed to quantum size effects that come into play when the particle size becomes comparable to the mean-free path of electrons in the metal. The theoretical curve shown in the figure was calculated using the experimentally-determined dielectric function of gold [24], which does not account for nonlocal effects due to surface scattering and electron spill-out. Recent quantum mechanical calculations have demonstrated the electron density at the particle surface drops from its maximum value (inside the particle) to its minimum value (outside the particle) over a distance comparable with the electron Fermi wavelength [7]. This effect, called "spill-out", is a direct consequence of the wave nature of the electron. Large clusters are not affected by this effect, thus the Mie theory predicts accurately predicts the resonance positions for clusters larger than 10 nm. But it will affect measurably the resonance plasma shifts for clusters smaller than approximately 5 nm. In the case of alkali metals this effect leads to a red-shifted plasma frequency as on decreasing the nanoparticle radii [7]. On the contrary, noble metal clusters exhibit the reversed trend, due to reduced s–d screening [7,25,26]. Tiggesbaumker et al., for instance, have provided calculations and experimental data for Ag cluster ions which show a clear blue shift of the resonance peak and reproduced the effect experimentally observed in the gas phase [25]. A spectral blue shift has been also observed from nanocomposite thin films of gold clusters embedded in a porous alumina

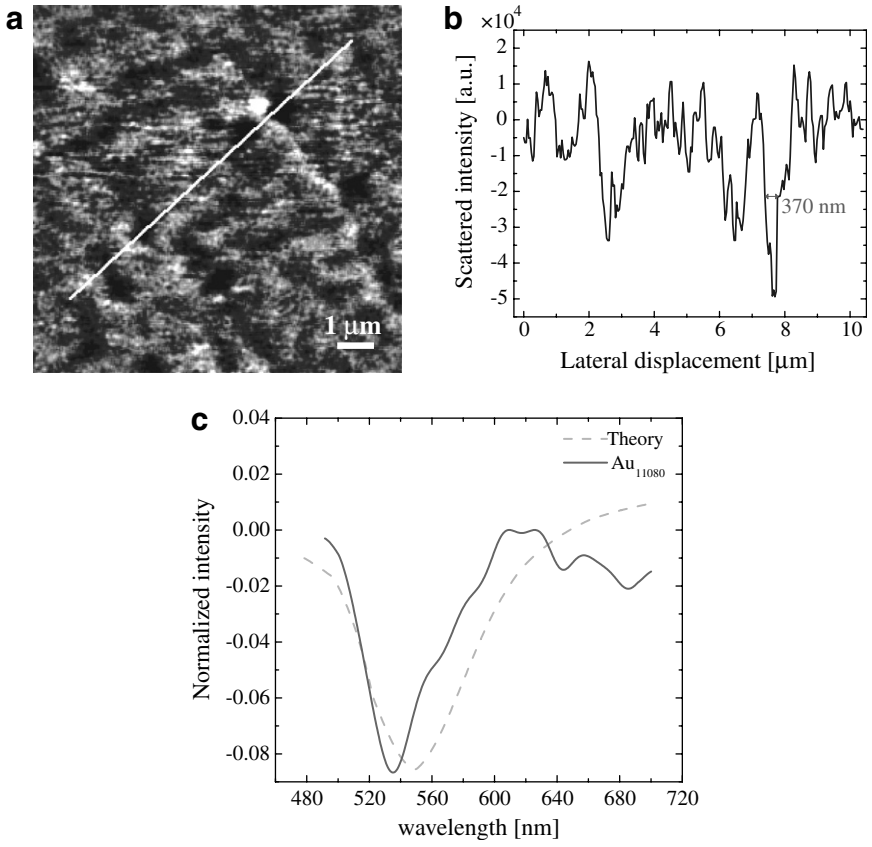

Fig. 3. (a) Intensity image of individual Au_{11080} clusters (7.7 nm) on glass in immersion oil; (b) corresponding intensity profile which shows the diffraction limited lateral resolution of the system. The black holes represent the clusters. (c) Plasmon spectrum of an individual Au_{11080} cluster on a PMMA coated quartz substrate. The comparison with the theoretical curve shows a clear blue shift.

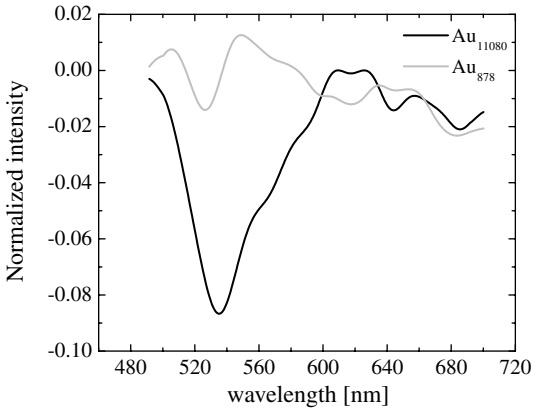

Fig. 4. Plasmon spectra of individual Au_{11080} and Au_{878} clusters on a PMMA coated quartz substrate. The curves show a pronounced blue shift as the cluster size becomes smaller.

matrix in the size range 2–7 nm by Prevel et al. [26], which is in agreement with our observations.

The small blue shift observed in the plasma resonance peak of individual Au_{11080} particles can thus be accounted for by the electron spill-out theory. We observed an even more pronounced blue shift for smaller clusters like Au_{878}. Fig. 4 shows corresponding spectra recorded for individual Au_{11080} particles (~7 nm) and Au_{878} particles (~3 nm) on PMMA coated quartz. The resonance peaks are measured to be at 535.3 nm for the Au_{11080} particle and at 526.6 nm for the Au_{878} particle.

A small shoulder was observed in the Au_{11080} spectrum (Fig. 3c) at ~562.4 nm. We speculate it is due to the slightly ellipsoidal shape of the cluster on the surface, as mentioned previously. For ellipsoidal particles, the polarizability is a function of the eccentricity of the particle, which gives shifted plasmon resonances along the main axes of the ellipsoid [27]. Using an unpolarised supercontinuum light source, it is expected to collect a plasmon resonance curve which is the envelope of the resonances along the main axes.

4. Conclusions

We measured the optical properties of single size-selected gold nanoparticles using an interferometric detection system. Plasmon resonance spectra of size-selected nanoparticles down to 3 nm in diameter were collected. The spectra show an evident blue shift compared to the theoretical calculations employing bulk dielectric constants. The blue shift is more prominent for small nanoparticles.

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