

Surface plasmon enhanced non-linear optical response of gold nanoparticles at the air/toluene interface

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Colloidal gold nanoparticles in toluene solution, synthesised using a two-phase liquid/liquid system, display second harmonic generation, wavelength analysis of which indicates the narrow frequency band of the gold surface plasmon for nanoparticles present at the air/toluene interface.

There is a great deal of interest in the preparation of simple thiol derivatised gold metal clusters of nanometre dimensions^{1–4} and more recently, in the synthesis of a new family of well defined compounds in which clusters of metal atoms are stabilised by groups carrying organic functionalities.^{5–7} Two aspects are of current interest, the chemistry of the stabilising groups and the electronic properties of the metal core, the size of which can be altered by the preparation conditions. The control of these properties is essential for the use of these compounds in the preparation of superlattices⁸ and other applications where the linking of nanoparticles can lead to complex structures with unusual electronic properties. Potential applications are in many fields such as chemical catalysis, molecular electronics or biosensors.⁹ Here, we report the use of surface second harmonic generation (SSHG)^{10,11} as a new technique for the characterisation of the noble-metal nanoparticles at air/liquid interfaces where the technique has been shown to be powerful, even in the non-resonant case.¹² This non-linear technique is highly sensitive to resonant plasmon excitation, which is observed for the first time for gold nanoparticles adsorbed at the air/toluene interface.

Colloidal gold nanoparticles were prepared using a two-phase (water/toluene) reduction of AuCl_4^- by sodium tetrahydroborate.¹³ The solution was stored in the dark at room temp. and the colloid did not show any signs of precipitation after several months. High-resolution TEM photographs of similar preparations gave an average particle diameter of 6 nm.¹³ The UV–VIS absorption spectrum of the Au solution presents a strong absorption band at λ_{max} ca. 530 nm. This prominent optical feature is attributed to plasmon oscillation modes of conduction electrons in the colloidal nanoparticles which are coupled to the applied electromagnetic field. Both the physical nature of this plasmon mode and its dependence on particle size and shape is well understood.^{14,15}

Second harmonic generation experiments were carried out at the air/toluene interface for the gold nanoparticles in toluene. Wavelength analysis of the second harmonic response from the gold particles adsorbed at the interface was performed with a nanosecond Nd^{3+} -YAG system pumping an optical parametric oscillator (Spectra-Physics, GCR170-10 pumping a MOP0 710) delivering pulses in the wavelength range 800–1200 nm, at a frequency of 10 Hz and of 5 ns duration. Pulse energy was kept below 1.5 mJ to avoid surface damage. The incident beam was collimated by a telescope and directed onto the air/toluene interface. The reflected SSHG signal generated in the visible range at each exciting wavelength was collected with a lens. It was then passed through IR filters to reject residual fundamental radiation, focused onto a monochromator and detected with a gated photon counter (recording of 50 s duration). The

frequency of the exciting laser was changed in steps between 800 and 1200 nm.

Fig. 1 shows the intensity of the second harmonic response as a function of the SSHG wavelength for a solution of gold nanoparticles. Toluene shows no absorbance between 800 and 1200 nm and as expected, negligible SSHG signal was observed from a pure toluene/air interface. In the presence of colloidal gold, the SSHG spectrum displays a strong resonance in the range 450–600 nm of the harmonic wavelength with a maximum of the SSHG resonance at 520 nm. The bandwidth and the maximum of the SSHG response are very similar to those observed in the absorption spectrum and hence, the SSHG spectrum clearly shows the narrow frequency band of the plasmon excitations caused by the Au nanoparticles adsorbed at the air/toluene interface. This enhancement arises from the coupling, through the surface, between the resonant local field of the incident light wave with the conduction electrons of the metal colloid.

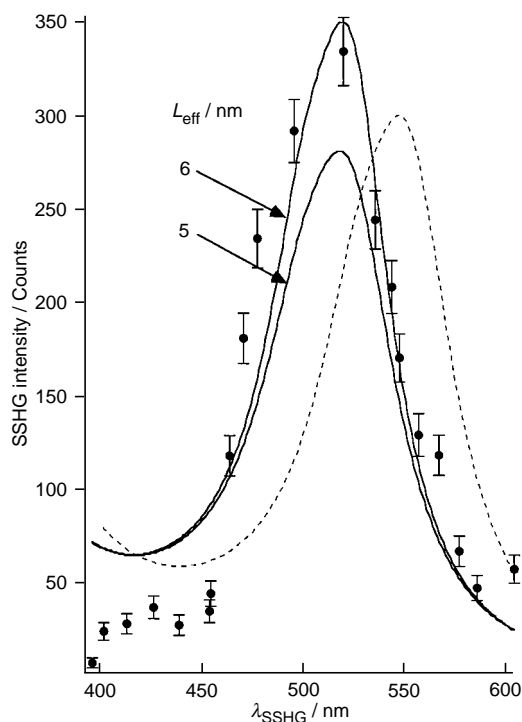


Fig. 1 SSHG spectrum for the underivatized gold nanoparticles at the air/toluene interface (circles). The adsorption band corresponds to surface plasmon excitations and has a maximum at 520 nm. The solid line represents the calculated SSHG spectrum, using eqn. (1) (term in brackets multiplied by ω^2) for gold nanoparticles in toluene taking size effects into account ($L_{\text{eff}} = 6$ and 5 nm). The solid line is for $\lambda_p = 138.5$ nm, corresponding to bulk gold; the dotted line is for a material with a free electron concentration 10% lower than that of bulk gold, for $\lambda_p' = 146$ nm and $v_f' = 1.342 \times 10^6$ m s⁻¹ (and $L_{\text{eff}} = 6$ nm).

The theory of second harmonic signal generation for metal spheres in the Mie approximation has been developed by Agarwal and Jha.¹⁶ At the plasmon resonance frequency, the term attributed to the surface non-linear polarization contribution dominates over the volume contribution, with a net enhancement compared to the non-resonant case. The output second harmonic power for spherical particles in vacuum is given by eqn. (1):¹⁶

$$S = \frac{3ce^2|E^{(i)}|^4}{m_e^2} \left(\frac{2R}{c}\right)^6 \omega^2 \left\{ \left| \frac{1 - \varepsilon(2\omega)}{[\varepsilon(\omega) + 2][\varepsilon(2\omega) + 2]} \right|^2 + \frac{36}{5} \left| \frac{\varepsilon(\omega) - 1}{[\varepsilon(\omega) + 2]^2 [2\varepsilon(2\omega) + 3]} \right|^2 \right\} \quad (1)$$

where $E^{(i)}$ is the intensity of the electric field at the surface, ε is the complex dielectric function of the particles, ω is the frequency of the exciting radiation, 2ω is the second harmonic frequency, m_e is the effective mass of the electron, R is the particle radius, c is the velocity of light and e is the electronic charge. For particles in a medium of relative permittivity ε_m , the dielectric function to be used in eqn. (1) is the permittivity relative to that of the medium, $\varepsilon_{rel} = \varepsilon/\varepsilon_m$.

In order to show qualitatively that the SSHG signal observed does correspond to the presence of colloidal gold at the interface, the dielectric function for particles of radius R was calculated following well established procedures.¹⁷ When the interband contribution is small compared with that due to core and free electrons, the complex dielectric function is given by eqn. (2):¹⁸

$$\varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\omega \left(\frac{1}{\tau_{bulk}} + \frac{v_f}{L_{eff}} \right)} \quad (2)$$

where ω_p is the bulk plasma frequency, ε_∞ is the dielectric contribution due to the atomic core polarizability, τ_{bulk} is the electron relaxation time in the bulk metal, v_f is the electron velocity at the Fermi level and L_{eff} is the effective electronic mean free path. Values of $\omega_p = 1.36 \times 10^{16} \text{ s}^{-1}$ ($\lambda_p = 138.5 \text{ nm}$), $v_f = 1.4 \times 10^6 \text{ m s}^{-1}$ and $\tau_{bulk} = 9.1 \times 10^{-15} \text{ s}$ were used in the calculations,¹⁸ ε_m for pure toluene was taken as 2.23. The dielectric function of gold employed was calculated from eqn. (2) taking a value of ε_∞ of 9.9 based on the data from Innes and Sambles.¹⁸ The data from Johnston and Christy¹⁹ leads to a value of 12.0. However, the differences between these and other values in the literature for the dielectric function of Au are due to the nature of the thin films used in the measurements, since other effects related to film thickness, crystallographic orientation and imperfections come into operation. Different values of ε_∞ lead to a shift in the position of the maximum in the SSHG signal but do not alter the features of the calculated wavelength dependence. The calculated second harmonic intensity functions, using eqn. (1) (term in brackets multiplied by ω^2), for gold nanoparticles in toluene, with 6 and 5 nm of effective electronic mean free path, are presented in Fig. 1. The agreement between experimental data and calculation for $L_{eff} = 6 \text{ nm}$ is very good. Fig. 1 also shows the effect of a decrease of 10% in the concentration of free electrons, highlighting the sensitivity of the technique to the electronic properties of the nanoparticles. For the calculation, we only consider that the change of the free electron density alters the bulk plasma frequency and the Fermi velocity ($\omega_p' = 1.29 \times 10^{16} \text{ s}^{-1}$, $v_f' = 1.342 \times 10^6 \text{ m s}^{-1}$).²⁰ Changing the free electron density may probably affect ε_∞ and τ_{bulk} , but since there is no straightforward relation with the free electron density, we use the same value already mentioned (*i.e.* $\varepsilon_\infty = 9.9$ and $\tau_{bulk} = 9.1 \times 10^{-15} \text{ s}$). Although the sample is not

monodisperse, from the point of view of a preliminary analysis of the experimental observations, the results shown in Fig. 1 represent a strong confirmation of the non-linear optical properties of Au nanoparticles present at the air/toluene interface.

To our knowledge, this is the first example of a SSHG resonance observed for solutions of nanosized metal particles. Previous SSHG work on colloidal metal particles was carried out by Efrima and coworkers.²¹ In this work silver metal liquid-like films were formed at the interface of immiscible liquids from large individual colloidal silver particles stabilised by detergents and shown to exhibit second harmonic signals. Gold nanoparticles are easily derivatised with functional ligands for the subsequent attachment of chromophores, redox labels or biomolecules.^{5,6} The optical SSHG technique described is a powerful method to investigate specific interfacial adsorption, and the electronic properties of chemically functionalised metal nanoclusters. The latter is of importance owing to the rapid advances in synthetic nanoparticles chemistry.⁶

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Footnote and References

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