Hyper-Rayleigh scattering in electrochemically synthesized Ag–Au coupled clusters

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Jagdish W Dadge[1]**, M Islam**[1]**, A K Dharmadhikari**[2]**, S R Mahamuni**[1] **and R C Aiyer**[1,3]

[1] Department of Physics, Laser Laboratory, University of Pune, Pune-411 007, India
[2] Department of Nuclear and Atomic Physics, Tata Institute of Fundamental Research, Mumbai 400 005, India

E-mail: rca@physics.unipune.ernet.in

Abstract
Electrochemically synthesized bimetallic (Ag–Au) nanoclusters (coupled) of average sizes of 6 and 12 nm were studied for coherent second harmonic generation (SHG) in different organic media. Significant enhancement in SHG intensity of these nanoclusters in toluene is observed due to its lower dielectric constant. By hyper-Rayleigh scattering (HRS) the β value is found to be 1.62×10^{-20} esu for 6 nm size coupled clusters, which is four to five orders of magnitude higher than that reported for gold particles.

1. Introduction

For many years the synthesis and physical properties of noble metal nanoclusters have been intensively investigated. The studies on bimetallic nanoparticles in colloidal form drew less attention, partly because of difficulties in synthesis. The bimetallic gold and silver nanoparticles in colloidal solution have been described on various occasions [1–10]. The enormous interest in metal nanoparticles is due to their unique optical properties, which arise from the collective oscillation of free conduction electrons due to the interaction with electromagnetic radiation [11]. Two metals combined to form nanoparticles are known as bimetallic nanoparticles. The optical properties of bimetallic clusters are governed by a combination of the dielectric functions of both the metals. Their combination strongly depends on the microscopic arrangement of the atoms within the particles, to form an alloy or core–shell or coupled nanoparticles. Bimetallic nanoparticles of various combinations of metals have been studied by several groups with a focus on the study of the optical [1], catalytic [2, 3], or non-linear properties [4]. In the case of gold and silver, formation of core–shell or coupled bimetallic clusters is difficult due to their nearly identical lattice constants, which leads to a strong tendency towards alloy formation. The colloidal Ag–Au alloys were studied in detail by Kim Joo [5], Bright *et al* [6], and Link *et al* [7] and the non-linear optical properties were

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[3] Author to whom any correspondence should be addressed.

studied by Philip *et al* [4]. Studies of core–shell Au/Ag were carried out by Schierhorn and Liz-Marzan [8], where the Au and Ag particles were separated by SiO_2 by chemical synthesis. Mulvaney *et al* [9] observed a red shift towards the absorption band of pure Au particles, when more Au was deposited on Ag cores. More recently, Mandal *et al* [10] reported the synthesis of core–shell bimetallic nanoparticles by the citrate reduction method for single molecule detection in solution using the surface enhanced Raman scattering (SERS) method.

The hyper-Rayleigh scattering is a nonlinear incoherent second order light scattering, which is used for studying the second order nonlinear optical (NLO) properties of molecules or nanoparticles in solution [12]. The generation of HRS is due to fluctuations of the density or orientation of molecules or nanoparticles, which instantaneously break the centrosymmetry of isotropic media and create conditions of net frequency doubling. The problem with the experimental determination of the second order NLO polarizability, β, lies in the fact that centrosymmetric structures of individual molecules with a nonzero microscopic hyperpolarizability, which do not possess a macroscopic second order NLO susceptibility B. Therefore, the first measurements of B were performed on crystals without centrosymmetry, Langmuir–Blodgett films and poled polymers [12, 13]. However, the Kurtz powder method generates a substantial number of second harmonic powder efficiency data [14]. Compared to the conventional technique of electric field induced second harmonic generation (EFISHG) [12] the HRS method offers advantages. In particular, it can be performed in a liquid phase without applying an electric field for alignment. Consequently, HRS has been successfully used to determine the β value of coupled nanoparticles. Semiconductor or metal nanoparticles exhibit interesting optical properties due to the confinement of the electronic wavefunctions, the drastically changing surface to volume ratio and their surface conditions [15].

In this paper, to the best of our knowledge, the first example of coupled Ag–Au bimetallic nanoparticles in the colloidal form synthesized by employing the simple electrochemical method and its β value is reported. These are found to be 4–5 orders of magnitude higher than that reported for gold particles [22]. The newly modelled bimetallic system establishes a relationship between the local electromagnetic field effect and the enhancement of SHG, which provides further insight into the enhancement mechanism of SHG.

2. Experimental details

The bimetallic coupled nanoparticles of 6 and 12 nm were prepared using the electrochemical method described by Reetz *et al* [16]. The process consists of two electrodes separated by 1 cm (optimized) set up for 50 ml electrolyte solution. A gold or silver sheet (1×1 cm^2) as an anode and a platinum sheet (1×1 cm^2) as a cathode were used. Tetraoctylammonium bromide (TOAB) (0.02 mol) in acetonitrile/THF (4:1) serves as the supporting electrolyte. The cross sectional current density of 20 mA to 40 mA cm^{-2} was applied under nitrogen environment and constant stirring. Quantitative dissolution of the anode occurs with the formation of nanoparticles. The dispersion was washed with acetronitrile for complete removal of the reaction by-products.

The present method is capable of yielding coupled nanostructures by varying the processing parameters. If silver nanoparticles are formed prior to those of gold, silver nanoparticles act as nuclei for growth of gold nanoparticles, which eventually give rise to the formation of coupled Ag–Au nanostructures.

Size estimation and structural studies of the nanoparticles were carried out by XRD using the copper Kα line ($\lambda = 1.54$ Å), as well as by TEM using a Philips CM 200 instrument, operated at 200 kV. SEM and EDS were employed for checking the purity of the synthesized particles.
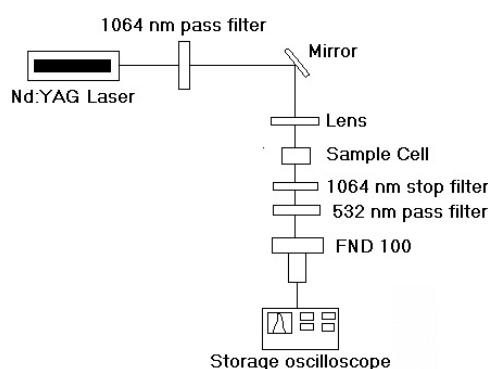
Figure 1. Experimental set-up for HRS and SHG.

The schematics of the experimental set-up for coherent SHG and HRS measurement is shown in figure 1, which consists of a Q-switched Nd:YAG laser ($\lambda = 1064$ nm) of 1–100 mJ pulse energy, 1 Hz repetition rate and 20 ns pulse width [17–20]. The laser radiation was filtered by a 1064 nm pass filter (Melles Griot) to minimize the background intensity. For coherent SHG the laser beam was focused on a $10 \times 10 \times 1$ mm^3 borosilicate cuvette using a lens (focal length 14 cm). The cuvette contains nanoparticles in the colloidal form. The signal generated in the visible range was detected through a monochromator with a photomultiplier tube after passing through a 1064 nm stop filter and a 530 nm pass filter and measured on a fast storage oscilloscope (THS 730A). The pulse width of the fundamental beam and the 2ω beam was found to be the same, confirming the second harmonic generation measured on an FND-100 with appropriate filters, and the coherence was confirmed by using a polarizer. The coherent SHG measurements of coupled nanoparticles were carried out for 6 and 12 nm sizes in different organic solvents. All the solvents were prechecked by the same experimental set-up as for SHG. None of the solvents showed SHG, as the solvents have no absorption between 300 and 1200 nm. In this case powder urea was used as the reference sample.

The HRS measurements of coupled nanoparticles with size of 6 nm were carried out in methanol by the methods described in [21–24]. The laser beam was focused on a $10 \times 10 \times 45$ mm^3 quartz cuvette using a lens (focal length 14 cm) containing the nanocrystallites in the colloidal form. The HRS signal generated was focused onto a detector (FND 100) after passing through a 532 nm pass filter (Melles Griot). The detector was placed at right angles to the fundamental beam. The HRS signal was measured using a Tektronix fast storage oscilloscope (THS 730A).

Figure 2 shows a representative TEM photograph of coupled Ag–Au nanoparticles. Here the average size of Ag–Au nanoclusters is 100 nm with a standard deviation of ± 2 nm. Ag and Au particles are seen side by side. The selective area diffraction pattern shows (figure 2 inset) the (111) and (200) planes of Ag and Au nanoclusters. The cappant is not seen in the TEM photograph as a separate shell because of its organic nature.

Figure 3 shows the x-ray diffraction patterns of 6 and 12 nm coupled particles. The diffraction patterns only show diffraction peaks for Ag–Au, which confirms the high purity and crystallinity in the electrochemically synthesized coupled nanoparticles.

3. Results and discussion

The interaction of small metal particles with the external electromagnetic field induced by a light wave results in a coherent oscillation of the conduction (free) electrons, called surface
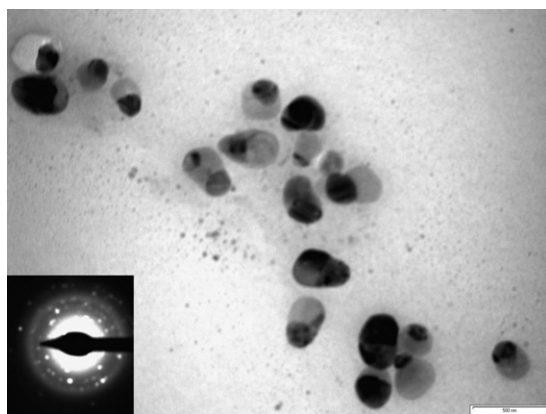
**Figure 2.** TEM image of coupled Ag–Au bimetallic nanoparticles.
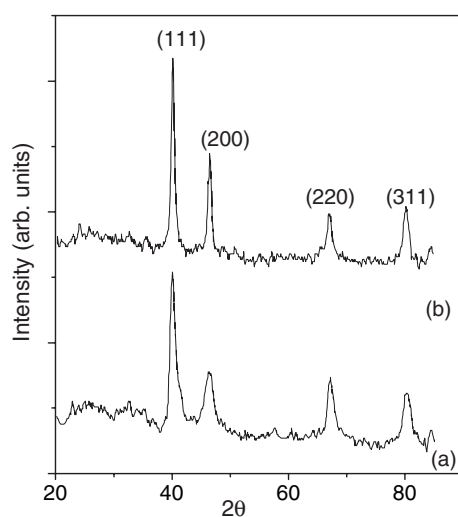
Figure 3. XRD pattern of Ag/Au coupled nanoparticles: (a) 6 nm and (b) 12 nm.

plasmon (SP) resonance. The size-dependent optical absorption cannot be predicted by Mie theory. However, it has been proved [11] empirically and widely accepted that varying the electron mean free path as well as the dielectric constant can yield optical absorption spectra that reasonably agree with the experimental values.

Figures 4(a) and (b) show two distinct SP absorption bands at 410 ± 5 nm, 520 ± 5 nm and at 420 ± 5 nm, 535 ± 5 nm for 6 and 12 nm Ag–Au coupled nanoparticles, respectively. These bimetallic structures comprise equal sized Ag and Au nanoparticles (figure 2). In other words, silver nanoparticles act as nuclei for growth of gold nanoparticles, to eventually give rise to coupled Ag–Au nanostructures.

The incoherent harmonic signal, known as the hyper-Rayleigh signal, scattered by the solution in the right angle direction to the fundamental incident beam has been detected from a monodispersed solution of nanoparticles.
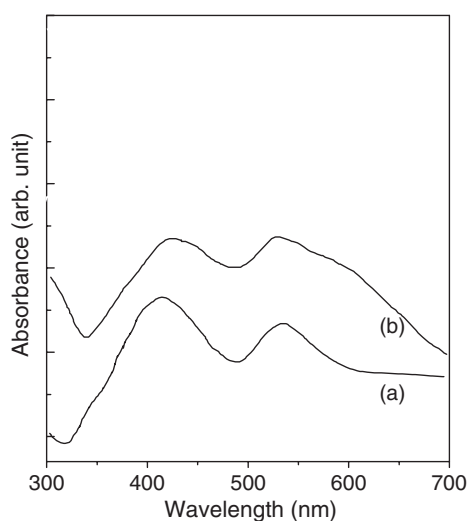
Figure 4. Optical absorption spectra of Au/Ag nanostructures of coupled nanoparticles having size (a) 6 nm and (b)12 nm.

A quadratic dependence of the HRS signal $I^{2\omega}$ on the incident light intensity I^{ω} is always observed, according to $I^{2\omega} = GB^2(I^{\omega})^2$, where G is a proportionality constant containing geometrical and electronic factors. For a two component system,

$$B^2 = N_{\text{solvent}}\beta^2_{\text{solvent}} + N_{\text{solute}}\beta^2_{\text{solute}}. \tag{1}$$

The low concentration of solute molecules does not significantly change the number density N_{solvent} of the solvent molecules. Measurements at different number densities of the solute then show a linear dependence of GB^2 on N_{solute}. From the intercept and the slope, β_{solute} is calculated [25–27] when β_{solvent} is known, or vice versa. Since no external field has been applied for directing the dipoles, the local field correction factor at zero frequency is eliminated. The local field correction factors are needed at optical frequencies, which can be estimated by the standard methods [13]. The internal reference method (IRM) eliminates the need for local field correction factors. These factors are divided out by calibrating and measuring in nearly the same local field as long as the number density of the solute molecules present does not significantly change the refractive index of the solution.

To ascertain that the results of our measurements are consistent with the accepted data, we have calibrated our experiment by using *para*-nitroaniline (*p*-NA) dissolved in methanol as the sample. The obtained value of β of *p*-NA was 9.1×10^{-30} esu, which was in satisfactory agreement with the literature value [28]. The quadratic dependence of the observed HRS signal $I^{2\omega}$ on incident intensity I^{ω} is illustrated in figure 5 for 6 nm size coupled nanoparticles in methanol. The expected linear dependence of the retrieved value for the quadratic coefficient GB^2 on the number density N_{solute} is shown in figure 6. The hyperpolarizability of a single bimetallic nanoparticle was obtained, provided the hyperpolarizability of a methanol molecule is known, which is $\beta_{\text{solvent}} = 0.69 \times 10^{-30}$ esu [29]. We were able to deduce the method of extracting accurate values for β_{solute} by the IRM. The obtained value for coupled bimetallic nanoparticle is $\beta_{\text{coupled}} = 1.62 \times 10^{-20}$ esu, which is four to five orders higher than that reported for gold particles $15.3 \pm 2.3 \times 10^{-25}$ esu [22]. This can be explained in terms of radiative dipole resonance [30]. Silver and gold nanoparticles are considered as dipoles (two plasmonic surfaces). Upon exposing to laser light, these dipoles may oscillate radiatively at the second
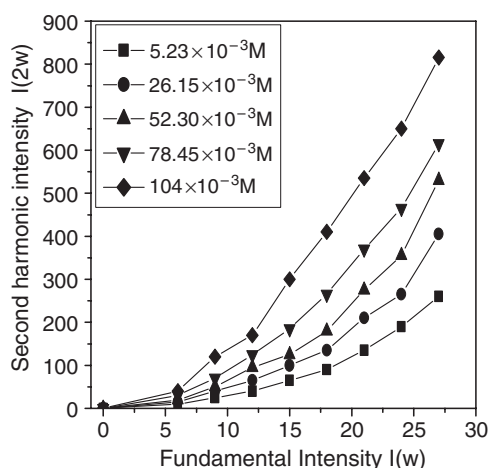
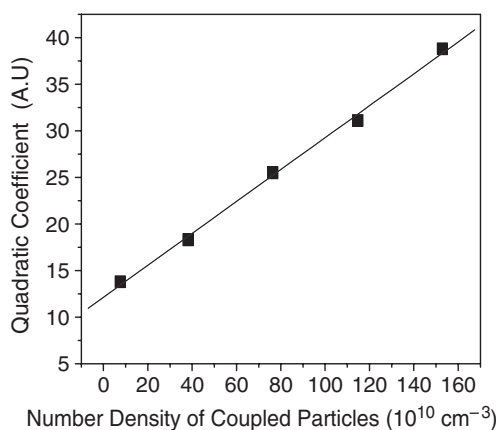**Figure 5.** Incoherent SHG in methanol for coupled nanoparticles.

Figure 6. Quadratic coefficient $GB^2 = G[N_{solvent}\beta_{solvent}^2 + N_{solute}\beta_{solute}^2]$, obtained from the curves in figure 5 versus N_{solute}, the number density of coupled nanoparticles in methanol.

harmonic of their fundamental. An anomalous field enhancement occurs in the vicinity of two plasmon resonance surfaces, which is reported theoretically and experimentally by Lalayan *et al* [31]. In the present case this contribution appears to be dominant. The percentage of Au and Ag in the bimetallic nanoparticles was found by atomic absorption spectroscopy (Chemito 201).

It is known that the HRS method relies upon random density fluctuations to create conditions compatible with the net frequency doubled. For each scatterer in solution, a substantial requirement for the finite HRS is the presence of non-centrosymmetric structure. The bimetallic nanoparticles studied here have cubic structure. However, the continuity of the crystalline lattice is broken at the surface nanoparticles. This results in their second order NLO response, which drastically differs from those of the corresponding nanocrystalline substance.

As reported, surface termination of the crystalline lattice creates a condition of non-centrosymmetry, which contributes to the large β values [32, 33]. The literature [34] also
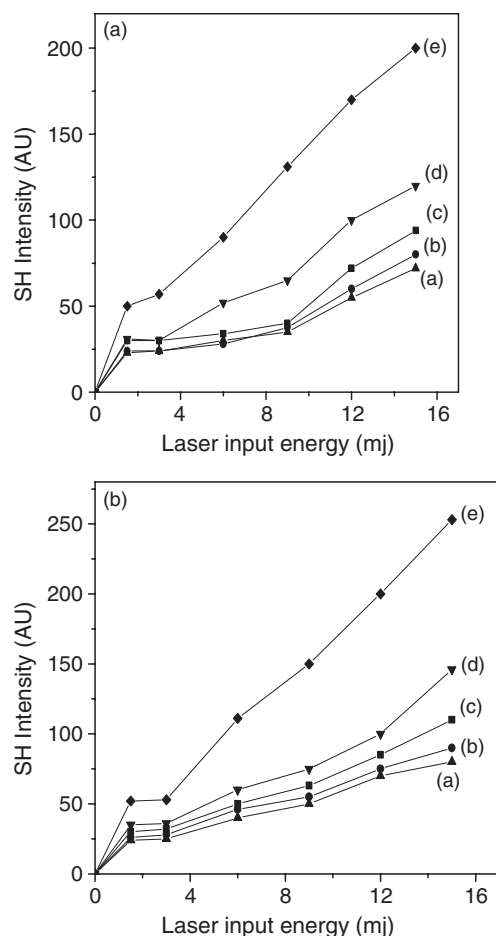
Figure 7. (a), (b) SHG of 6 and 12 nm coupled Ag/Au bimetallic nanoparticles respectively in (a) DMSO, (b) DMF, (c) acetonitrile, (d) ethanol and (e) toluene.

indicated that the electron distribution around the surface atoms is inherently highly non-centrosymmetric. Moreover an important feature of nanoscale particles is the enhanced ratio of the surface atoms to volume atoms. This shows that nanoparticle surface atoms play an important role in the contribution to the HRS signal.

The SHG intensity of the coupled nanoparticles (figures 7(a) and (b)) in toluene is much higher than that in acetonitrile, ethanol, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) because of the lower dielectric constant of the medium. It plays an important role in generating the observed SHG. The medium with low dielectric constant (toluene, 2.3) gives higher SHG power (from equation (2)). The enhancement in SHG can be attributed to the ratio of ac (optical frequency) to dc dielectric constant that represents the dielectric losses in the medium. The higher the ratio, the lower are the losses in the medium. The dielectric losses in toluene (0.94) are the lowest. The dielectric constant relation for the solvents is toluene < ethanol < acetonitrile < DMF < DMSO.

Figures 7(a) and (b) show SHG of 6 and 12 nm size Ag–Au coupled nanoparticles in different solvents. The SHG intensity varies as a square of the input intensity. It is clear

that the SHG intensity increases with the size, which is due to the volume contribution of the nanoparticles i.e. the radius of the particles, which is directly proportional to the SHG power as per equation (2).

The theory of second harmonic signal generation for a metal sphere in the Mie approximation has been developed by Agarwal and Jha [35]. 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 of second harmonic power for the spherical particles is given by

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

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 radius of the particle, 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 the equation is the permittivity relative to that of the medium $\varepsilon_{rel} = \varepsilon/\varepsilon_m$.

In the case of nanoparticles with a diameter much smaller than the wavelength of the incident light, the second harmonic can be generated because of the quadrupole moment contribution, which is generally very weak and can be enhanced because of the local field resonance corresponding to the surface plasmon excitation of the particles. When spherical particles of dielectric constant $\varepsilon_m = \varepsilon_1 + i\varepsilon_2$ are immersed in a continuum medium of dielectric constant ε_s subjected to a quasi-static electric field E_0, the electric field inside the particles is given by $E_i = \frac{3\varepsilon_s}{\varepsilon_m + 2\varepsilon_s} E_0$, when $\varepsilon_m \approx -2\varepsilon_s$ resonance occurs and the electric field inside the particle is enhanced.

To our knowledge, this is the first example of SHG and HRS observation of TOAB protected Ag–Au coupled nanoparticles synthesized by the simple electrochemical route. The change of dielectrics also changes the intensity of SHG because of the dielectric function [36] and electron density of solvents.

4. Conclusion

In conclusion, coupled bimetallic nanoparticles using the electrochemical method are successfully synthesized. Using the HRS technique, large second order NLO response of the coupled bimetallic nanoparticles was exhibited. The coupled $\beta_{coupled}$ 1.62×10^{-20} esu in methanol is calculated. These predict considerable potential of coupled nanoparticles in NLO applications. Coupled nanoparticles for two sizes exhibit SHG in different media.

Acknowledgments

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