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Second Harmonic Response of Gold Nanorods: A Strong Enhancement with the Aspect Ratio

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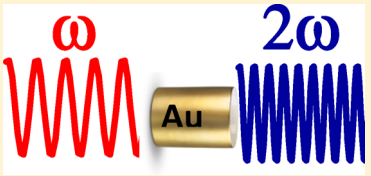
Supporting Information

ABSTRACT: Nonlinear optical properties of gold nanorods of different aspect ratios synthesized by radiolysis were studied by harmonic light scattering (HLS). A strong enhancement of the second harmonic response with respect to the aspect ratio, together with a relative increase of dipolar hyperpolarizability, is reported.



SECTION: Plasmonics, Optical Materials, and Hard Matter

Gold nanoparticles (AuNPs) typically have dimensions ranging from 1 to 100 nm. AuNPs are attracting increasing attention because of their unique physical, chemical, electrical, and optical properties. AuNPs are widely used in chemistry as catalysts and polymer additives;[1,2] in biology as sensors, for imaging and cancer therapy; and in nanoscale electronics.[3−7] The AuNPs are promising materials for optoelectronics and nonlinear optics. The collective excitation of conduction electrons in these NPs under the action of electromagnetic waves and the subsequent enhancement of the local field trigger various optical resonance phenomena in a broad spectral range.[8,9] Such effects can be used in optical data storage, subwavelength optical devices, nonlinear optical switches and optical limiters.[10−12] In particular, gold nanorods (AuNRs) display exceptional optical properties. Indeed, these nanorods (NRs) present two surface plasmon resonances (SPR) corresponding to the electromagnetic-wave-driven oscillation of the quasi-free electrons along (longitudinal SPR or LSPR) and perpendicular (transverse SPR or TSPR) to the long rod axis. Whereas the TSPR spectral response is almost insensitive to the NRs morphology, the wavelength corresponding to the longitudinal one can be tuned from green to near-infrared by increasing the nanorod aspect ratio (AR) (the aspect ratio being the ratio of the largest axis on the shortest one): the higher the AR, the higher the LSPR wavelength.

It has been shown that the first hyperpolarizability (β) of gold colloids depends strongly on the particle diameter.[13] Second harmonic generation (SHG) from individual gold spherical nanoparticles has been recently reported,[14] but for relatively large (150 nm) particles. Various experimental studies have been reported on the exaltation of quadratic nonlinear optics (NLO) properties of molecular units by gold nanostructures. Exaltation of (SHG) from ultrathin dye layers deposited on fractal gold surfaces has been reported.[15] A SHG signal of individual molecules in the presence of very small gold NPs (1 nm) has been evidenced in the context of biological membrane imaging.[16] The hyperpolarizability (β) of particles dispersed in solution is usually measured using the harmonic light scattering (HLS) technique.[17,18] Large β values have been reported for 5−55 nm SiO_2,[19] copper,[20] silver[21,22] and gold nanoparticles.[13,14,21−24] In spite of the importance of study of nonlinear properties of NPs and their applications, only one publication reported the β measurement of a nanorod using HLS.[23] However, in this paper the authors used nanorods mainly to act as biosensors, rather than for the investigation of their NLO properties as such. In particular, they did not report any comparison between nanorods and spherical nanoparticles, and they did not investigate the effect of their aspect ratio on their NLO properties.

In this Letter, we report for the first time the influence of the aspect ratio on the optical second harmonic response of AuNRs. Spherical gold nanoparticles and gold nanorods were synthesized by one pot radiolytic synthesis in the presence of cetyltrimethylammonium bromide (CTAB) (and silver ions in case of AuNRs)[25] (Figure S1 in the Supporting Information). Solvent radiolysis induces the formation of solvated electrons and radicals which reduce metal ions homogeneously in the medium, resulting in a homogeneous nucleation. Small and relatively monodisperse nanoparticles are obtained. From TEM images of each sample and considering at least 100 nanoparticles, we evaluated the average particle size and ARs of NRs (Figure S2 in the Supporting Information). The UV−vis absorption spectra of the different solutions are shown in Figure 1. Table 1 gives the size, AR, and linear and nonlinear optical properties of our gold NSs and NRs (Table S1 in the Supporting Information).

HLS measurements were performed at 1.06 μm according to a procedure described in detail in refs 17 and 18 and in the

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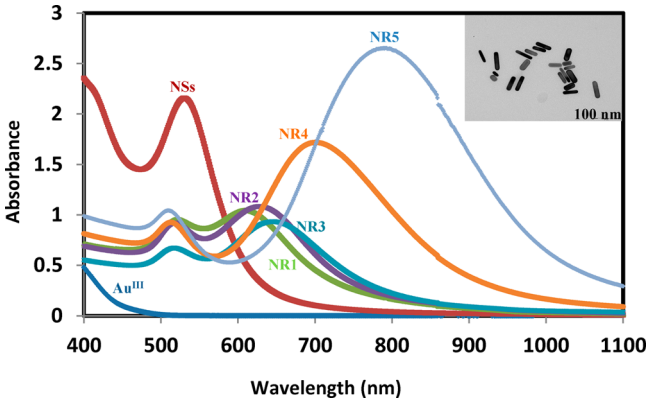

Figure 1. UV−visible absorption spectra of Au^{III} solution ($HAu^{III}Cl_4$ 2 × 10^{-3} M) (before irradiation), Au Nanospheres and Au Nanorods of different aspect ratio (synthesized with different amounts of $AgNO_3$ (NR1:1 × 10^{-5} M; NR2: 2 × 10^{-5} M; NR3: 3 × 10^{-5} M; NR4: 4 × 10^{-5} M; NR5: 5 × 10^{-5} M), dose =32.2 kGy, optical path length =2 mm. Inset: TEM image of Au NR5.

Table 1. Maximum Wavelengths of Linear Absorbance λ_{max}, Aspect Ratio and Average Diameter, First Hyperpolarizability (β) of Au Per Particle, Depolarization Ratio (D) of AuNSs and AuNPs, and Squared Value of the Nonlinear Anisotropy ρ

AuNPs	λ_{max} (transversal/ longitudinal) (nm)	aspect ratio	diameter (nm)	β/ particle 10^{-26} esu	D	ρ^2
Au^{III}						
NSs	530	1	6.3	0.35	0.44	5.1
NR 1	522, 611	1.7	15	2.6	0.33	2.3
NR 2	519, 628	1.9	13.5	3.2	0.30	1.8
NR 3	517, 645	2.5	12.6	3.7	0.28	1.5
NR 4	512, 700	2.7	12	4.2	0.25	1.2
NR 5	511, 788	3.8	11	5.0	0.22	0.84

Supporting Information. The scattered harmonic signal from a solution is given by

$$I^{2\omega} = g(N_s\langle\beta_s^2\rangle + N\langle\beta^2\rangle)I_\omega^2$$

where g is a geometry factor, N_s and N are the number of solvent molecules and nanoparticles per unit volume respectively; β_s and β are the molecular hyperpolarizability of the solvent and nanoparticle, respectively. From the slopes P (respectively P_0) of the lines obtained for the solution (respectively solvent) from the variation of $I^{2\omega}$ as a function of $I_{NPP}^{2\omega}$, the ≪reference≫ SHG intensity from a reference NLO material (NPP) sample, we can infer the β values of the nanoparticles.

Due to the significant absorption of AuNPs at 532 nm, the second harmonic intensity of the solution must be corrected from its absorbance (A) at this wavelength, by multiplying it by a correction factor 10^A. This 10^A factor accounts for the losses due to linear absorption of the scattered light by the solution at 532 nm and is determined from the UV−Vis spectra. We have explored the possibility of two-photon fluorescence phenomena in the nanoparticle solutions, by recording the spectrum of the scattered signal. As the incoming intensity is modest, we did not observe any significant broadband luminescence signal around the second harmonic emission. Then β of gold nanospheres (NSs) and nanorods (NRs) can be directly inferred from HLS measurements. We have also measured the $\beta_{Au^{III}}$ value of the Au^{III} complex ($AuCl_4^-$) precursor used to synthesize the NSs and NRs. This "molecular" hyperpolarizability is small ($\beta_{Au^{III}}$ = 8 × 10^{-30} esu). These values are presented in Table 1.

It is observed that β per nanoparticle increases from the sphere to the rod shape, and continuously increases with the AR of the NRs, as shown in Figure 2, even when the number of

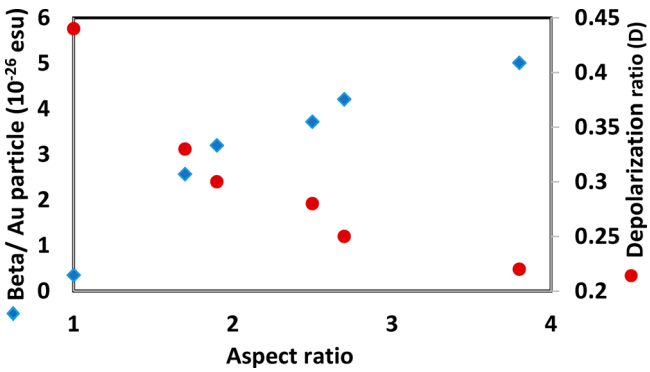

Figure 2. Plot of the absolute values of the first hyperpolarizability β calculated per Au nanoparticle in solution and of the depolarization ratio (D) versus the aspect ratio of AuNRs.

gold atoms per particle remains almost the same, as for NR3, NR4, and NR5. The increase of β with AR is therefore not related to the number of atoms. Brevet et al. also reported that the HLS intensity collected from a solution of a mixture of gold nanorods and nanospheres in water solution confirms that the HLS signal mainly arises from the nanorods.[26] As mentioned above, the authors of ref 23 did not investigate the role of AR on the NLO response of nanorods.

We have also performed variable incident polarization experiment using HLS in order to determine the nonlinear anisotropy of the particles. The depolarization ratio D is plotted as a function of the AR of the AuNPs (Figure 2). D decreases with the increase the AR. In other words, as the length of the NRs increases, the D ratio decreases, which clearly evidences an increase of the anisotropic behavior.

In an earlier work, a depolarization ratio has been reported as D = 0.47 ± 0.03 for 20 nm AuNPs. The authors concluded that the HLS signal was of dipolar origin.[12,27] For 6.3 nm AuNSs we found D = 0.44, confirming this ≪dipolar≫ contribution to β even for nanospheres. However, even for relatively low D values, an octupolar contribution to the β tensor must be taken into account, as shown by Brasselet and Zyss.[28] In the following, we shall see that this octupolar contribution is still dominant in NSs and decreases in NRs when increasing AR.

The simple expression of D as a function of the nonlinear anisotropy ρ is expressed as

$$D = \frac{\langle\beta_{2,ZXX}^2\rangle}{\langle\beta_{2,XXX}^2\rangle} = \frac{1}{9}\frac{7 + 12\rho^2}{7 + 2\rho^2}$$

We may infer from D measurement and from $\langle\beta^2\rangle$ the value of $\rho = \|\beta_{J=3}\|/\|\beta_{J=1}\|$ and the intrinsic $\|\beta_{J=1}\|$ and $\|\beta_{J=3}\|$ components. The maximum depolarization for pure octupoles ($\rho = \infty$) is D_{max}= 2/3 and the minimal depolarization for dipoles ((ρ = 0) is D_{min} = 4/27 = 0.148. The squared dipolar ($\|\beta_{J=1}\|^2$) and octupolar ($\|\beta_{J=3}\|^2$) norms of the dipolar and octupolar β tensor components are then calculated and plotted

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in Figure 3 and their values are mentioned in Table S2 in the Supporting Information. Both dipolar and octupolar responses

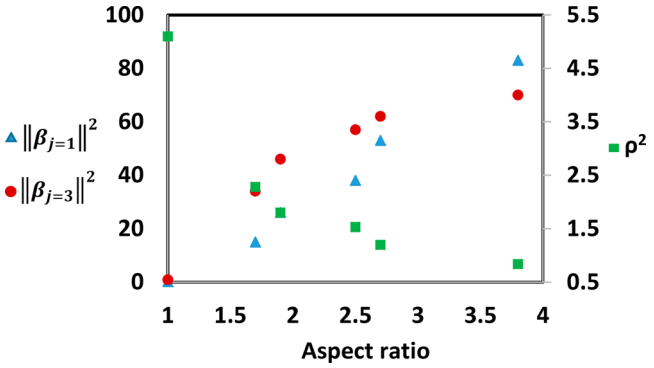

Figure 3. Plot of the squared norms of the dipolar and octupolar tensor components of NRs (Units 10^{-52} (esu) ^{2}), along with their squared NLO anisotropy (ρ^2) with respect to their aspect ratio.

increase with the AR, and their ratio decreases as displayed in Figure 3.

It may be surprising to observe these high hyperpolarizability values in centrosymmetric objects. As our nanorods are very small objects, much smaller that the optical wavelengths involved in the NLO phenomena, a quadrupolar contribution to the β tensor is not expected. However, some authors have shown that a significant HLS response can be obtained from centrosymmetric nanoscale electron-rich objects such as conjugated molecules.[30,31] The study performed by Honeybourne[31] on centrosymmetric anilinosquaraine dyes using the SCF-PPP-CI method showed that these molecules may exhibit high β values due to charge distortion of conjugated electrons by an adjacent polar moiety, such as polar solvent molecules. These internal charge distortions result in an instantaneous noncentrosymmetric electron distribution that contribute to the HLS signal.

Another work by Yaliraki and Silbey[30] showed that centrosymmetric objects may display a significant HLS response by taking into account vibrational transitions and solvent effective field contribution. This latter interpretation (solvent effect) comes closer to that of Honeybourne (ref 31), in spite of the fact that Yaliraki and Silbey do not consider an internal deformation of the electronic cloud, but the contribution of the external local field E_{loc} induced by the solvent to a second harmonic generation signal via a γE_{loc} term involving a third-order hyperpolarizability γ.

In our case, due to the high sensitivity of gold electrons to external effects, we think that the interpretation of Honeybourne could be more adequate to describe the emergence of a SHG signal. In analogy with these models applied to electron-rich one-dimensional molecules, we may consider that, in rod-like structures, the electron distribution is less isotropic than in a sphere, and NRs may behave like dipolar-like instantaneous "plasmonic molecules", with increasing values of β when increasing the length of the object. It must be pointed-out that the depolarization ratio becomes rather weak for NRs, and displays the same value as for the standard dipolar reference DR1 NLO molecule.[29] Au nanorods seem to behave like giant dipolar nonlinear molecules, at least when their β tensor is measured using the HLS technique, which takes into account the SH contributions from instantaneous charge distortions in nanoparticles.

It must be pointed-out that this increase of the NR β values with increasing aspect ratio cannot be accounted for by the effects of wavelength dispersion resulting in resonances between the TSPR and/or LSPR bands and the photons at ω or 2ω. In fact, using a combination of two 2-level dispersion equations applied to LSPR and TSPR, respectively, we expect a significant relative decrease of the β values when increasing the aspect ratio, as discussed in the Supporting Information.

Therefore, these experiments emphasize the strong enhancement of the second harmonic response from the sphere to the rod shape and its continuous increase with the aspect ratio, together with a relative increase of dipolar hyperpolarizability. The result of the dipolar hyperpolarizability clearly evidences an increase of the anisotropic behavior. These NLO nanostructures offer very interesting perspectives in the domain of ultrasensitive detection[23] and imaging methods. Further studies will focus on the functionalization of AuNRs with different NLO dyes, and on the insertion of gold NRs into polymer matrices in order to investigate their NLO properties in a solid-state matrix, and to try to detect second harmonic generation of a single nanorod by confocal NLO microscopy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization and analysis of data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far below 0 °C. *Chem. Lett.* **1987**, 405−408.

(2) Haruta, M.; Yamada, N.; Kobayashi, T.; Ijima, S. Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide. *J. Catal.* **1989**, *115*, 301−309.

(3) Daniel, M. C.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2004**, *104*, 293−346.

(4) Jain, P. K.; El-Sayed, I. H.; El-Sayed, M. A. Review of Some Interesting Surface Plasmon Resonance-Enhanced Properties of Noble Metal Nanoparticles and Their Applications to Biosystems. *Nanotoday* **2007**, *2*, 107−118.

(5) Gole, A.; Murphy, C. J. Seed-Mediated Synthesis of Gold Nanorods: Role of the Size and Nature of the Seed. *J. Chem. Mater.* **2004**, *16*, 3633−3640.

(6) Abidi, W.; Remita, H. Light-Driven Reactions and Materials in the Environmental Technology. *Recent Pat. Eng.* **2010**, *4*, 170.

(7) Jana, N. R.; Gearheart, L.; Murphy, C. J. Wet Chemical Synthesis of High Aspect Ratio Cylindrical Gold Nanorods. *J. Phys. Chem. B* **2001**, *105*, 4065−4067.
(8) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer-Verlag, Berlin, 1995.
(9) Stepanov, A. L.; Hole, D. E. Fabrication of Metal Nanoparticles in Sapphire by Low-Energy Ion Implantation. *Recent Res. Dev. Appl. Phys.* **2002**, *9*, 109−129.
(10) Krenn, J. R. Nanoparticle Waveguides: Watching Energy Transfer. *Nat. Mater.* **2003**, *2* (4), 210−211.
(11) Barnes, W. L.; Dereux, A.; Ebbesen, T. W. Surface Plasmon Subwavelength Optics. *Nature* **2003**, *424* (6950), 824−830.
(12) Nappa, J.; Revillod, G.; Russier Antoine, I.; Benichou, E.; Jonin, C.; Brevet, P. F. Electric Dipole Origin of the Second Harmonic Generation of Small Metallic Particles. *Phys. Rev. B.* **2005**, *71* (165407), 1−4.
(13) Galletto, P.; Brevet, P. F.; Girault, H. H.; Antoine, R.; Broyer, M. Size Dependence of the Surface Plasmon Enhanced Second Harmonic Response of Gold Colloids: Towards a New Calibration Method. *Chem. Commun.* **1999**, *7*, 581−582.
(14) Butet, J.; Duboisset, J.; Bachelier, G.; Russier-Antoine, I.; Benichou, E.; Jonin, C.; Brevet, P. F. Optical Second Harmonic Generation of Single Metallic Nanoparticles Embedded in a Homogeneous Medium. *Nano Lett.* **2010**, *10*, 1717−1721.
(15) Anceau, C.; Brasselet, S.; Zyss, J.; Gadenne, P. Local Second-Harmonic Generation Enhancement on Gold Nanostructures Probed by Two-Photon Microscopy. *Opt. Lett.* **2003**, *28* (9), 713−715.
(16) Peleg, G.; Lewis, A.; Linial, M.; Loew, L. M. Nonlinear Optical Measurement of Membrane Potential around Single Molecules at Selected Cellular Sites. *Proc. Natl. Acad. Sci. U. S. A.* **1999**, *96*, 6700−6704.
(17) Terhune, R. W.; Maker, P. D.; Savage, C. M. Measurements of Nonlinear Light Scattering. *Phys. Rev. Lett.* **1965**, *14*, 681−684.
(18) Clays, K.; Persoons, A. Hyper-Rayleigh Scattering in Solution. *Phys. Rev. Lett.* **1991**, *66*, 2980−2983.
(19) Vance, F. W.; Lemon, B. I.; Ekhoff, J. A.; Hupp, J. T. Interrogation of Nanoscale Silicon Dioxide/Water Interfaces via Hyper-Rayleigh Scattering. *J. Phys. Chem. B* **1998**, *102*, 1845−1848.
(20) Chandra, M.; Indi, S. S.; Das, P. K. Depolarized Hyper-Rayleigh Scattering from Copper Nanoparticles. *J. Phys. Chem. C* **2007**, *111* (28), 10652−10656.
(21) Johnson, R. C.; Li, J.; Hupp, J. T.; Schatz, G. C. Hyper-Rayleigh Scattering Studies of Silver, Copper, and Platinum Nanoparticle Suspensions. *Chem. Phys. Lett.* **2002**, *356*, 534−540.
(22) Russier-Antoine, I.; Benichou, E.; Bachelier, G.; Jonin, C.; Brevet, P. F. Second Harmonic Generation from Silver and Gold Nanoparticles. *J. Phys. Chem. C* **2007**, *111*, 9044−9048.
(23) Darbha, G. K.; Rai, U. S.; Singh, A. K.; Ray, P. S. Gold Nanorod-Based Sensing of Sequence-Specific HIV-1 Viris DNA by Using Hyper-Rayleigh Scattering Spectroscopy. *Chem.—Eur. J.* **2008**, *14*, 3896−3903.
(24) Vance, F. W.; Lemon, B. I.; Hupp, J. T. Multipolar contributions of the Enormous Hyper-Rayleigh Scattering from Nanocrystalline Gold Particle Suspensions. *J. Phys. Chem. B* **1998**, *102*, 10091−10093.
(25) Abidi, W.; Selvakanan, P. R.; Guillet, Y.; Lampre, I.; Beaunier, P.; Pansu, B.; Palpant, B.; Remita, H. One-Pot Radiolytic Synthesis of Gold Nanorods and Their Optical Properties. *J. Phys. Chem. C* **2010**, *114*, 14794−14803.
(26) Nappa, J.; Revillod, G.; Abid, J.-P.; Russier-Antoine, I.; Jonin, C.; Benichou, E.; Girault, H. H.; Brevet, P. F. Hyper-Rayleigh Scattering of Gold Nanorods and Their Relationship with Linear Assemblies of Gold Nanospheres. *Faraday Discuss.* **2004**, *125*, 145−156.
(27) Duboisset, J.; Matar, G.; Russier-Antoine, I.; Benichou, E.; Bachelier, G.; Jonin, C.; Ficheux, D.; Besson, F.; Brevet, P. F. First Hyperpolarizability of the Natural Aromatic Amino Acids Tryptophan, Tyrosine, and Phenylalanine and the Tripeptide Lysine−Tryptophan−Lysine Determined by Hyper-Rayleigh Scattering. *J. Phys. Chem. B* **2010**, *114*, 13861−13865.
(28) Brasselet, S.; Zyss, J. Multipolar Molecules and Multipolar Fields: Probing and Controlling the Tensorial Nature of Nonlinear Molecular Media. *J. Opt. Soc. Am. B* **1998**, *15* (1), 257−288.
(29) Brasselet, S.; Zyss, J. Relation between Quantum and Geometric Dimensionalities in Molecular Nonlinear Optics: Beyond the Two-Level Model for Anisotropic System. *J. Nonlin. Phys. Mater.* **1996**, *5* (4), 671−693.
(30) Yaliraki, S. N.; Silbey, R. J. Hyper-Rayleigh Scattering of Centrosymmetric Molecules in Solution. *J. Chem. Phys.* **1999**, *111*, 1561−1568.
(31) Honeybourne, C. A Mechanism for Strong SHG by Centrosymmetric Anilinosquaraine Dyes. *Adv. Mater.* **1999**, *11*, 1477−1480.