Article

Quadratic Electro-Optic Effect in Metal Nanoparticles in a Transparent Dielectric Medium

Mrinal Thakur * and Justin Van Cleave

Photonic Materials Research Laboratory, Auburn University, Auburn, AL 36849, USA;
vanclea@tigermail.auburn.edu

* Correspondence: mthakur@eng.auburn.edu

Received: 8 December 2018; Accepted: 7 January 2019; Published: 10 January 2019

Abstract: The quadratic electro-optic effect/Kerr coefficients were measured for the first time for metal nanoparticles. In particular, gold nanoparticles in glass were studied. Measurements were made using the field-induced birefringence method at a wavelength near the onset of the surface plasmon resonance. The magnitudes of the Kerr coefficients for different sizes of gold nanoparticles in glass were measured and compared with that of subnanometer size metallic particles in non-conjugated conductive polymers. The magnitude of the Kerr coefficient was found to increase rapidly (about d^{-3}) when the diameter, d , of the nanoparticles was decreased. This is consistent with the existing theories and understanding of nonlinear optics in metal nanoparticles. The results imply a broad range of new applications of metal nanoparticles in electro-optic switching/modulation, low-cost Kerr cells and other uses in optoelectronics.

Keywords: quadratic electro-optic effect; metal nanoparticles; nonlinear optics; Kerr coefficient

1. Introduction

Nonlinear optics in metal nanoparticles within transparent dielectric media has been studied extensively [1–12]. In particular, third order optics using ultrashort (femtosecond) laser pulses in such metal nanoparticle systems have been widely studied and reported. The metallic nanoparticles of smaller diameters (<about 10 nm) are also called quantum dots since many of their properties can be understood by considering the quantum confinement of the electrons within nanometer dimensions. The third-order susceptibilities ($\chi^{(3)}$) and response times of various metallic nanoparticles in dielectric media have been measured for different diameters of nanoparticles. However, as our literature review revealed no measurement of the quadratic electro-optic effect in such systems has been published or is known in the prior art and no correlation between third order susceptibility and particle size have been established. Using high intensity, short pulse, second order optical effect has been shown for specific nanoparticles utilizing the asymmetry in the shapes/interfaces [12]. Second order optics has no relevance to the quadratic electro-optic effects presented here. Quadratic electro-optic effects have applications in ultrafast electro-optic modulation/switching and also as Kerr cells, Kerr-gates for mode-locking, Q-switching, and other applications in optoelectronics.

The focus of the present report is on the measurement of quadratic electro-optic/Kerr effects in metal nanoparticles of various sizes with an objective of further elucidating the mechanisms of nonlinear optics in these important systems. The quadratic electro-optic effect is given by: $\Delta n = K\lambda E^2$, where Δn is the change in the refractive index (induced birefringence), K is the Kerr coefficient, λ is the wavelength and E stands for the applied electric field. Thus a change in the refractive index occurs when an electric field is applied. This change in the refractive index leads to electro-optic switching/modulation and any related device application. The larger the Kerr coefficient is, the larger the change in the refractive index for any given electric field and optical path length through the sample.

Since the magnitude of K is typically small in these samples (as will be shown in the following), a long, up to about 4 cm, sample was used to obtain detectable electro-optic modulation signal. Such samples are difficult to come by and that is probably part of the reason such measurements have not previously been made or reported. The advantage of making these measurements compared to four-wave mixing or optical Kerr effect with ultrashort optical pulses is that thermal contribution is expected to be minimal in the quadratic electro-optic measurements. This is because the metal nanoparticles in glass are insulators that allow no detectable or only an extremely small electrical current and, thus, lead to minimal thermal effects. Therefore, these measurements may provide evidence of a correlation of nonlinearity with particle size, while such a correlation could be obscured by thermal effects in the other nonlinear optical measurements involving intense laser pulses.

2. Experimental Section

Glass samples (dimensions of about $4\text{ cm} \times 4\text{ cm} \times 3\text{ mm}$) containing gold nanoparticles of specific diameters were purchased from a commercial vendor. These samples were characterized using optical absorption spectroscopy and the wavelengths of the surface plasmon resonances (abbreviated SPR) were determined. Using the surface plasmon resonances and the relative peak intensities, the particle sizes were determined using established procedures [4,7]. These samples were used for the measurement of the quadratic electro-optic/Kerr coefficients at a specific wavelength.

Metal electrodes were applied to the gold nanoparticle in-glass samples. An ac (alternating current) field at 4 kHz was applied to these electrodes using a power supply. The quadratic electro-optic measurements were made using the field-induced birefringence method (Figure 1) [13–19]. Briefly, the measurement was made as follows: A He–Ne laser (wavelength 633 nm) was used in these measurements since this wavelength is near the onset of the optical absorption due to surface plasmon resonance. Therefore, at this wavelength enhanced magnitudes of the Kerr coefficient could be expected. The laser beam was polarized at 45° with respect to the applied electric field and passed through the sample. The transmitted beam was passed through an analyzer which was cross-polarized with respect to the polarizer and the final beam was detected by a photo-detector (photodiode). A lock-in amplifier (with $2f$ synchronization) and an oscilloscope were used to record the modulation signals. The modulation signal was recorded for various applied ac electric fields and was found to depend quadratically on the applied electric field. The Kerr coefficients were determined from the observed modulations, applied fields and interaction path lengths within the samples, at a given wavelength.

Figure 1. Experimental set-up for measurement of quadratic electro-optic effect/Kerr coefficient.

3. Results and Discussion

Three glass samples containing gold nanoparticles of three different average particle diameters were studied and discussed in the following.

Samples of gold nanoparticles in glass (plates with dimensions: $4\text{ cm} \times 4\text{ cm} \times 3\text{ mm}$) were purchased from a commercial vendor. The optical absorption spectrum was recorded for light travelling

through the thickness of the sample plate. The size of the gold nanoparticle was estimated from the wavelength of the absorption peak (surface plasmon resonance) and the relative peak intensity, using the results published in the literature [4,7]. The absorption peak appeared at shorter wavelengths and the relative intensity of the peak decreased for smaller nanoparticles. For Sample 1 (Figure 2), the peak was at about 534 nm wavelength which corresponded to a particle diameter of about 50 nm. The results of the quadratic electro-optic measurement of Sample 1 are given in Figure 3. For Sample 2, the peak was at about a 527 nm wavelength which corresponded to a particle diameter of about 25 nm. For Sample 3 (Figure 4), the peak was at about 520 nm wavelength which corresponded to a particle diameter of about 15 nm. The relative peak intensities (absorbance at SPR divided by absorbance at ~400 nm) were also used, if needed, to ascertain the nanoparticle sizes [4].

Figure 2. Surface plasmon resonance spectrum of gold nanoparticles in glass (Sample 1, peak at 534 nm) with a particle diameter of about 50 nm.

Figure 3. Quadratic electro-optic modulation data for different applied electric fields, for a particle diameter of about 50 nm.

Figure 4. Surface plasmon resonance spectrum of gold nanoparticles in glass (Sample 3, peak at about 520 nm) with a particle diameter of about 15 nm.

Quadratic electro-optic measurements were made in these plates using the electric field-induced birefringence method discussed earlier. The beam at 633 nm from a He–Ne laser was passed through the long dimension (4 cm) of the plate. The results of the measurements are shown in Figures 3 and 5 for Samples 1 and 3 having particle diameters of about 50 nm and 15 nm respectively. The Kerr coefficients, as determined from the observed modulation signals, were about $2.5 \times 10^{-15} \text{ m/V}^2$, $2.0 \times 10^{-14} \text{ m/V}^2$ and $7.5 \times 10^{-14} \text{ m/V}^2$, respectively, for samples 1, 2 and 3. Under the same experimental conditions no detectable modulation was observed for glasses without metal nanoparticles. Considering previous reports, subnanometer size metallic-like particles were obtained in non-conjugated conductive polymers doped with iodine. [13–19] A charge–transfer from an isolated carbon–carbon double bond to the dopant creates highly confined metallic domains/quantum dots (surface plasmon resonance of about 400 nm and radical cation of about 300 nm). The subnanometer size particles have shown the largest known Kerr coefficients and two-photon absorption coefficients of any material. The Kerr coefficient is about $3.5 \times 10^{-10} \text{ m/V}^2$ at 633 nm for iodine-doped trans-polyisoprene [18,19]. All the magnitudes of the Kerr coefficient stated here are for the same optical density (about 0.05 at 633 nm).

Figure 5. Quadratic electro-optic modulation data for different applied electric fields, for a particle diameter of about 15 nm.

As these results show, the Kerr coefficient (K) increases rapidly as particle size decreases. The increase is roughly d^{-3} , where d is the nanoparticle diameter. Therefore, we may write the following equation: $K = K_0 d^{-3}$, where K_0 is the Kerr coefficient for $d = 1 \text{ nm}$. A plot of $\log K$ vs. $\log d$ is shown in Figure 6. It shows a slope of about -3 implying a d^{-3} dependence of the Kerr coefficient.

Figure 6. Kerr coefficient correlated with diameter of metallic nanoparticle.

This correlation between optical nonlinearity and d can be explained using an earlier theoretical treatment of metal nanoparticles in dielectric media [3]. According to this theory, $\chi^{(3)}$ increases as d^{-3} .

The Kerr coefficient (**K**) is proportional to $\chi^{(3)}(\omega; \omega, 0, 0)$. In particular, **K** is proportional to the real part of $\chi^{(3)}$. The measurements reported here were made at 633 nm which is near the onset of the surface plasmon resonance. Therefore, $\chi^{(3)}$ at this wavelength is complex, with real and imaginary parts. The theoretical treatment mentioned above predicts that the maximum value of $\chi^{(3)}$ is proportional to $T_1 T_2 (1 - d/d_0)/d^3$, where T_1 is the excited state lifetime, T_2 is the dephasing time, d_0 is a characteristic threshold diameter of the system and d is the diameter of the nanoparticle. Therefore, $d < d_0$, $\chi^{(3)}$ increases as d^{-3} . Although the particle concentration was not known for our samples, the optical density (αl) was similar (about 0.05 at 633 nm). The particle concentration would alter α the same way it would alter **K**. As long as the optical density was kept the same, we could compare the Kerr coefficients at the fundamental level. As the results show, the Kerr coefficient follows the theory and increases as d^{-3} . An alternative interpretation of the d^{-3} dependence is that for any given excitation the fraction of electrons excited in a nanoparticle is higher in a smaller particle since the total number of electrons in a smaller nanoparticle is lower. Therefore, a larger optical nonlinearity can be expected in a smaller nanoparticle [20].

This report provides the first experimental demonstration of the fundamental correlation between third order nonlinearity and the size of metal nanoparticles. It was not possible to demonstrate this correlation earlier, presumably because of thermal effects, which could be significant in other nonlinear optical measurements that utilized ultrashort intense optical pulses. These measurements include time-resolved four-wave mixing and optical Kerr effects using femtosecond pulses. Those measurements have produced a wealth of information, including excited-state lifetime, dephasing time, multiphoton processes and many others, although the effect of particle size was not clearly delineated. Use of intense optical pulses may excite interband transitions in gold nanoparticles and, according to theory, does not lead to any particle size dependence. Only intraband transitions involving surface plasmons are expected to show a particle size dependence of $\chi^{(3)}$, as observed here.

These metal nanoparticles within glass materials are expected to have various applications in ultrafast electro-optic switching/modulation, Kerr cells and others. Although the present results are for metal nanoparticles in glass, the results can be extended to metal nanoparticles in other transparent dielectric media.

4. Conclusions

Quadratic electro-optic effects (Kerr coefficients) were measured for the first time for metal nanoparticles within a transparent dielectric medium. In particular, gold nanoparticles in glass were studied. The measurements were made using a field-induced birefringence method. The magnitudes of the Kerr coefficients for the different sizes of gold nanoparticles in glass were measured and compared with that of subnanometer size metallic particles in non-conjugated conductive polymers. The magnitude was found to rapidly increase (about d^{-3}) for smaller diameters (d) of nanoparticles. The results are consistent with existing theories and understandings of nonlinear optics in metal nanoparticles. This size dependence was not previously observed in experiments, presumably because of thermal effects. In the present measurements, the thermal effect was insignificant. These results imply a broad range of applications of metal nanoparticles in ultrafast, electro-optic, modulation/switching, low-cost Kerr cells and other important functions in lasers and optoelectronics.

Author Contributions: Conceptualization, supervision, M.T.; experimental investigation, J.V.C.; writing, M.T.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhang, Y.-X.; Wang, Y.-H. Nonlinear optical properties of metal nanoparticles: A review. *RSC Adv.* **2017**, *7*, 45129–45144. [[CrossRef](#)]
2. Kim, K.-H.; Husakou, A.; Herrmann, J. Linear and nonlinear optical characteristics of composites containing metal nanoparticles of different sizes and shapes. *Opt. Exp.* **2010**, *18*, 7488. [[CrossRef](#)] [[PubMed](#)]
3. Hache, F.; Ricard, D.; Flytzanis, C. Optical nonlinearities of small metal particles: surface-mediated resonance and quantum size effects. *J. Opt. Soc. Am. B* **1986**, *3*, 1647. [[CrossRef](#)]
4. Haiss, W.; Thanh, N.T.K.; Aveyard, J.; Fernig, D.J. Determination of size and concentration of gold nanoparticles from uv-vis spectra. *Anal. Chem.* **2007**, *79*, 4215–4221. [[CrossRef](#)] [[PubMed](#)]
5. Van Cleave, J.; Thakur, M. Quadratic Electro-optic Effect in Nanometallic particles in Glass; Comparison with Iodine-doped Nonconjugated Conductive Polymers. *Bull. Am. Phys. Soc.* **2017**, *62*, K36.
6. Inouye, H.; Tanaka, K.; Tanahashi, I.; Hirao, K. Femtosecond optical Kerr effect in the gold nanoparticle system. *Jpn. J. Appl. Phys.* **1998**, *37*, L1520. [[CrossRef](#)]
7. Link, S.; El-Sayed, M. Spectral properties and relaxation dynamics of surface plasmon electronic oscillations in gold and silver nanodots and nanorods. *J. Phys. Chem. B* **1999**, *103*, 8410–8426. [[CrossRef](#)]
8. Ballesteros, J.M.; Serna, R.; Solis, J.; Afonso, C.N.; Petford-Long, A.K.; Osborne, D.H.; Haglund, R.F., Jr. Nonlinear Optical Physics and Applications of The Plasmonic Response in Metal Nanoparticles. *Appl. Phys. Lett.* **1997**, *71*, 2445. [[CrossRef](#)]
9. Pincon-Roetzing, N.; Prot, D.; Palpant, B.; Charron, E.; Debrus, S. Large optical Kerr effect in matrix-embedded metal nanoparticles. *Mater. Sci. Eng. C* **2002**, *19*, 51. [[CrossRef](#)]
10. Magruder, R.H., III; Yang, L.; Haglund, R.F., Jr.; White, C.W.; Yang, L.; Dorsinville, R.; Alfano, R.R. Optical Properties of Gold Nanocluster Composites. *Appl. Phys. Lett.* **1993**, *62*, 1730–1732. [[CrossRef](#)]
11. Tanahashi, I.; Yoshida, M.; Manabe, Y.; Tohda, T.; Sasaki, S.; Tokizaki, T.; Nakamura, A. Preparation and Nonlinear Optical Properties of Ag/SiO₂ Glass Composite Thin Films. *Jpn. J. Appl. Phys.* **1994**, *33*, L1410–L1412. [[CrossRef](#)]
12. Mendoza, I.R.; Rojo, R.R.; Rodriguez-Fernandez, L.; Oliver, A. Second order nonlinear response of composites containing aligned elongated silver nanoparticles. *Opt. Exp.* **2011**, *19*, 21575. [[CrossRef](#)] [[PubMed](#)]
13. Thakur, M. New Additions to Nonconjugated Conductive Polymers; Nonlinear Optical Effects. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2009**, *46*, 1185–1190. [[CrossRef](#)]
14. Thakur, M.; Swamy, R.; Titus, J. Quadratic Electro-optic Effect in a Nonconjugated Conductive Polymer. *Macromolecules* **2004**, *37*, 2677–2678. [[CrossRef](#)]
15. Rajagopalan, H.; Vipra, P.; Thakur, M. Quadratic Electro-optic Effect in a Nano-optical Material based on the Nonconjugated Conductive Polymer, Poly(β -pinene). *Appl. Phys. Lett.* **2006**, *88*, 033109. [[CrossRef](#)]
16. Titus, J.; Thakur, M. Two photon absorption in quantum dots based on a nonconjugated conductive polymer. *Appl. Phys. Lett.* **2007**, *90*, 121111. [[CrossRef](#)]
17. Narayanan, A.; Thakur, M. Quadratic electro-optic effect in the nonconjugated conductive polymer iodine-doped poly(β -pinene) measured at longer wavelengths including 1.55 μ m. *Solid State Commun.* **2010**, *150*, 375–378. [[CrossRef](#)]
18. Shrivastava, S.; Thakur, M. Quadratic Electro-optic Effect in the Nonconjugated Conductive Polymer iodine-doped trans-polyisoprene, an organic nano-metallic system. *Solid State Commun.* **2011**, *151*, 775–777. [[CrossRef](#)]
19. Shrivastava, S. Study of structures, quadratic electro-optic effect and rechargeable battery characteristics of specific nonconjugated conductive polymers including trans-1,4-polyisoprene. Master's Thesis, Auburn University, Auburn, AL, USA, 2011.
20. Thakur, M. Correlation between nonlinear optics in polydiacetylene and line-width in super-resolved fluorescence microscopy. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2016**, *53*, 188. [[CrossRef](#)]