Nonlinear refractive index of electric field aligned gold nanorods measured with a Hartmann-Shack wavefront aberrometer

Melissa Maldonado,1 Leonardo de S. Menezes,1 Leonardo F. Araujo,2 Greice K. B. da Costa,3 Isabel C. S. Carvalho,2 Jake Fontana,4 Cid B. de Araujo,1 and Anderson S. L. Gomes1

1) Departamento de Física, Universidade Federal de Pernambuco, Recife-PE, 50670-901, Brazil
2) Department of Physics, Pontifícia Universidade Católica do Rio de Janeiro (PUC-RIO), Rio de Janeiro, 22451-900, Brazil
3) Departamento de Física, Universidade Federal Rural do Rio de Janeiro, Seropédica-RJ, 23.897-000, Brazil
4) Naval Research Laboratory, 4555 Overlook Ave. Washington, D.C. 20375, U.S.A

(Dated: date; Received textdate; Revised textdate; Accepted textdate; Published textdate)

We report on the nonlinear refractive index of colloidal gold nanorods in organic suspensions as a function of electric field induced alignment applied along the laser propagation direction. The nonlinear optical experiments were carried out using a high repetition rate femtosecond laser and a Hartmann-Shack wavefront aberrometer in a collimated beam configuration. We find that the nonlinear refractive index of the gold nanorods is proportional to the orientational order parameter, which can be understood by a thermally induced nonlinear response. We also show the magnitude of the nonlinear response can be varied by 80%. The capability to rapidly modulate the nonlinear refractive index of these plasmonic suspensions may lead to innovative nonlinear optical nanotechnologies.

The unique nonlinear optical properties of plasmonic nanoparticles hold significant promise for developing innovative optical materials and devices. The nonlinear response of these materials may be well suited for chemical and biological sensing, optical limiters and switches, and nanoscale light sources. Moreover, the potential to dynamically control the nonlinear response of these materials is a key element to opening up advanced application spaces.

Recently, external electric fields were demonstrated to dynamically control the orientational order and in turn the linear optical response of suspensions of plasmonic nanorods at visible and near infrared wavelengths. The color tunable suspensions enabled fast switching times and large signal modulations.

However, the nonlinear response of such dynamic systems is not well characterized or understood. Padilha et al. demonstrated the influence of alignment on the nonlinear refractive index, \( n_2 \), by partially orienting gold nanorods in organic suspensions with electric fields using a femtosecond Z-scan technique, reporting \( n_2 \) values ranging from \( 7.8 - 5.0 \times 10^{-15} \, \text{cm}^2/\text{W} \) between the isotropic to partially aligned states.

To quantify the degree of electric field induced nanorod alignment in the present study, an aqueous suspension of gold nanorods with length= 75 nm and diameter= 25 nm were acquired commercially (Nanopartz, A12-25-700). The nanorods were coated with a polymer shell (Polymer Source, thiol-terminated polystyrene, \( M_n = 50k \)), to enable the nanorods to be suspended in toluene and aligned using electric fields. To eliminate solvent evaporation, preventing density changes, the nanorods were phase transferred once more into an oil (Cargille index matching fluid, \( n_D = 1.47 \)). The oil (2 ml) was placed into a 5 ml glass vial. Then 2 ml of the nanorod suspension (\( \sim 2 \, \text{nM} \)) was gently placed on top of the oil. The vial was placed in a fume hood for 2 days, allowing the toluene to completely evaporate, dispersing the nanorods into the oil.

Figure 1(a) is the experimental setup to characterize the electric field induced alignment of the gold nanorods. The nanorod-oil suspension was placed into a cuvette (C), composed of two 1 mm thick microscope slide glued together with a 1 mm glass spacer. On the outside of each microscope slide indium tin oxide (ITO) electrodes were chemically etched and served as electrodes to apply the electric field across the suspension. To prevent dielectric breakdown of the air while applying the electric field, the cuvette was submerged into a tank (O) of transformer oil (Lubrax AV 24), with a thickness of 34 mm. The voltage (V) was applied to the cuvette using a sinusoidal function generator (SRS DS345, 60 Hz) coupled to a 2000x voltage amplifier (Trek 20/20C). The entire alignment system (S) is then comprised of the suspension, cuvette, transformer oil and voltage supply. Simulations of the system were carried out using COMSOL Multi-physics to calculate the electric field inside the cuvette for a given applied voltage. From the simulations a relationship of \( E = 556V \) was retrieved. An unpolarized white light (WL) source (Ocean Optics HL-2000-LL) was used to probe the nanorod suspension in the geometry shown in Figure 1(a), where the wavevector of the probe light is parallel to the applied electric field direction. The light was collected into a spectrometer (SP, Ocean Optics HR4000).

---

1) Electronic mail: anderson@df.ufpe.br
FIG. 1. (a) Experimental nanorod alignment setup. (b) Absorption spectra of the gold nanorod suspension as a function of applied voltage. (c) Absorption at the longitudinal absorption peak (774 nm) versus applied voltage. (d) Absorption at the longitudinal absorption peak as a function of orientational order parameter, S

\[ \alpha = A + BS \]  

(1)

where A and B are constants and

\[ S = \frac{\int_{0}^{1} \frac{1}{2} (3 \cos^2(\theta) - 1) e^{(\frac{E}{E_c})^2 \cos^2(\theta)} d(\cos(\theta))}{\int_{0}^{1} e^{(\frac{E}{E_c})^2 \cos^2(\theta)} d(\cos(\theta))} \]  

(2)

\( \theta \) is the angle between the long axis of the nanorod and the applied electric field, \( E \), direction and \( E_c \) is the critical electric field needed to align the nanorods. The experimentally measured \( \alpha \) at the longitudinal peak wavelength as a function of \( E \) is fit to Eq. (1), determining the parameters \( A, B \) and \( E_c \), using a least square fitting algorithm. Figure 1(d) shows the absorption at the longitudinal peak wavelength versus the orientational order parameter, demonstrating that the linear absorption of the nanorods is proportional to the orientational order parameter for these nanorod-oil suspensions.

While the linear response of the nanorods as function of orientational order has been established, the nonlinear response versus alignment is not well understood. To investigate this relationship, the nonlinear refractive index of the gold nanorods was measured using the experimental setup depicted in Figure 2(a). The alignment system (S) described in Fig. 1(a) was used to align nanorods using electric fields. The nanorods, as a function of alignment, were probed with a Ti:sapphire laser (Coherent Mira, 800 nm, 150 fs, 76 MHz). The laser light first enters a halfwave plate (\( \lambda/2 \)), then through a Glan-Laser polarizer (GL) to control the incident power. Telescoping lenses (T1) were used to reduce the diameter of the laser beam to probe the nanorod suspension in the cuvette. A second telescoping lens set (T2) were used to expand the laser light to illuminate the entire CCD detector of a Hartmann-Shack wavefront aberrometer (HSWA, Thorlabs WFS150C).

The HSWA is a CCD consisting of groups of \( i \times j \) arrays (bins). In front of the CCD there is a microlens array, with one microlens per bin. Each microlens focuses the incident light into the center of the respective bin. A computer code checks the position of the microlens focus for each bin, as well as the light intensity into each bin. The code then reconstructs the beam wavefront based on the position and intensity of light in each bin using a set of orthogonal Zernike polynomial functions. The second radial order Zernike polynomial, \( Z_{2}^{0} \), is related to the wavefront focusing/defocusing and therefore to the intensity of the laser light.
FIG. 2. (a) Experimental setup to determine the nonlinear refractive index of the nanorods with a Hartmann-Shack wavefront aberrometer in a collimated beam configuration. (b) $Z_0^{cs_2}$ versus laser peak intensity for CS$_2$. (c) $Z_0^{oil}$ versus laser peak intensity for Cargille oil. (d) $\Delta n_2^{oil} = n_2^{th}(V) - n_2^{th}(V = 0)$ versus applied voltage for Cargille oil.

\[ Z_0^\theta = \left( \frac{2\pi L_{eff} n_2}{f\lambda} \right) I \]

(3)

where $I$ is the laser peak intensity, $L_{eff} = (1 - \exp(-\alpha L))/\alpha$ is the effective path length, $\lambda$ is the wavelength of light and $f$ is a dimensional constant related to the Zernike polynomial. From Eq. (3), by measuring $Z_0^\theta$ versus $I$ and resulting slope, the nonlinear refractive index, $n_2$, can be determined.

To determine $f$ in Eq. (3), a neat solution of CS$_2$, which has a well defined $n_2 = -3.1 \times 10^{-15}$ cm$^2$/W at 800 nm was placed inside a 2 mm path length cuvette and $Z_0^{cs_2} |_{CS_2}$ was measured as a function of laser intensity, by controlling the pulse energy. From the resulting slope in Figure 2(b), $f$ is calculated to be $1.5 \times 10^{-3}$.

To remove the possible nonlinear contribution from the oil, $Z_0^{oil}$ was measured as a function of laser intensity with pure oil (without nanorods) as shown in Figure 2(c). The nonlinear refractive index of the oil without a voltage applied was calculated using Eq. (3) to be $n_2^{th}(V = 0) = -6.2 \times 10^{-15}$ cm$^2$/W. The negative value indicates that the nonlinear refractive index is of thermal origin.

At a fixed laser intensity ($I = 4.5 \times 10^5$ W/cm$^2$), a voltage was applied across the cuvette ranging from $V = 0$ to $12$ kV, yielding a $n_2^{th}(V)$ at each voltage. The change in the nonlinear refractive index as a function of voltage, $\Delta n_2^{th} |_{oil} = n_2^{th}(V) - n_2^{th}(V = 0)$, is reported in Figure 2(d). These results demonstrate that the nonlinear refractive index of the oil is negative and do not change with applied voltage.

The relationship between the nonlinear refractive index and the orientational order of the nanorods is unknown. However, since the nonlinear refractive index of the nanorods is predominantly thermally induced due to the high repetition rate of the laser, then the response should depend on the optical absorption of the nanorods. Therefore the nonlinear refractive index of the nanorods is posited to depend linearly on the orientational order parameter,

\[ n_2^{th} = A + BS \]

(4)

To investigate how the nonlinear refractive index depends on the orientational order of the nanorods, $Z_0^{oil}$ was measured at a fixed intensity ($I = 4.5 \times 10^5$ W/cm$^2$) as a function of applied voltage. The nanorod contribution was then calculated by $Z_0^{oil} |_{nanorod} = Z_0^{oil} - Z_0^{oil} |_{oil}$ at each voltage (right hand side, Fig. 3(a)) and from this the variation of nonlinear refractive index was determined, $\Delta n_2^{th} |_{nanorod} = n_2^{th}(V) - n_2^{th}(V = 0)$, for the nanorods versus applied voltage (left hand side, Fig. 3(a)).

From Fig. 3(a) the thermal nonlinear refractive index of the nanorods as function of applied electric field was fit using the same algorithm from Eq. (1). Figure 3(b) validates the relationship in Eq. (3). The nonlinear refractive index of the nanorods depends linearly on the orientational order parameter.
FIG. 3. (a) The Zernike polynomial, $Z_{22}^{\text{n} \text{an} \text{or} \text{od}} = Z_{22}^{\text{n} \text{an} \text{or} \text{od}} - Z_{22}^{\text{o} \text{il} \text{d}},$ for the nanorods as a function of applied voltage at a fixed intensity of $I = 4.5 \times 10^5 \text{ W/cm}^2$ at 800 nm, right hand side. The nonlinear refractive index of the nanorods was calculated from $Z_{22}^{\text{n} \text{an} \text{or} \text{od}}$ using Eq. (3), left hand side. (b) The nonlinear refractive index of the nanorods at 800 nm as a function of the orientational order parameter, where $A = 0 \text{ m}^{-1}$, $B = 8.6 \times 10^{-14} \text{ m}^{-1}$ and $E_c = 1.2 \text{ V} \cdot \text{m}^{-1}$ The solid red line is a linear fit.

In conclusion, we showed using a high repetition rate femtosecond laser and a Hartmann-Shack wavefront aberrometer that the thermally induced nonlinear refractive index of electric field aligned plasmonic nanorods is proportional to the orientational order parameter. We also show the magnitude of the nonlinear response can be varied by 80%. These results provide a straightforward means to predict and understand the nonlinear response of these materials as a function of orientational order, which may lead to nonlinear optical modulator applications.

This work was supported by the National Institute of Photonics (INFo) project. The support from the Conselho Nacional de Desenvolvimento Científico e Tecnológico-CNPq and Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco-FACEPE is acknowledged. I.C. and A.G. acknowledge support by the Office of Naval Research Global under ONRG-NICOP-N62909-16-1-2180. J.F. thanks the Office of Naval Research for support.

1 N. Jiang, X. Zhuo, and J. Wang, Chemical Reviews (2017), 10.1021/acs.chemrev.7b00252.
2 H. Chen, L. Shao, Q. Li, and J. Wang, Chemical Society Reviews 42, 2679 (2013).
3 J. Fontana, G. K. B. da Costa, J. M. Pereira, J. Naciri, B. R. Ratna, P. Palfy-Muhoray, and I. C. S. Carvalho, Applied Physics Letters 108, 081904 (2016).
4 S. Etcheverry, L. F. Araujo, G. K. B. da Costa, J. M. B. Pereira, A. R. Camara, J. Naciri, B. R. Ratna, I. Hernandez-Romano, C. J. S. de Matos, I. C. S. Carvalho, W. Margulis, and J. Fontana, Optica 4, 864 (2017).
5 L. A. Padilha, J. P. Fontana, D. Kohlgraf-Owens, M. F. Moreira, S. Webster, P. Palfy-Muhoray, P. G. Kik, D. J. Hagan, and E. W. V. Stryland, in 2009 Conference on Lasers and Electro-Optics and 2009 Conference on Quantum Electronics and Laser Science Conference pp. 1–2.
6 D. Rativa, R. E. de Araujo, A. S. L. Gomes, and B. Vohnsen, Optics Express 17, 22047 (2009).
7 M. Reichert, H. Hu, M. R. Ferdinandus, M. Seidel, P. Zhao, T. R. Ensley, D. Peceli, J. M. Reed, D. A. Fishman, S. Webster, D. J. Hagan, and E. W. Van Stryland, Optica 1, 436 (2014).