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Aspect-ratio Dependence of Optical Nonlinearities on Resonance with Longitudinal Surface Plasmon in Au Nanorods: Unique Character versus Common Behavior

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Abstract

Unique character and common behavior are two distinguished things. In frontier nanoscience and nanotechnology, unique characters were normally obtained in some novel exotics materials such as metal-metal core-shell materials, metallic-semiconducting hybrid nanomaterials, and organic-inorganics complex nano-compounds. On the other hand, normal behavior of natural phenomena including in nano-size objects were obviously predicted based on their exact size related to confinement effect, and capability to interact with another physical system in nature. Here, we report an example of unique character due to evolution nonlinear behavior observed in gold nanorod with their aspect-ratio dependence of optical nonlinearities investigated by femtosecond Z-scan measurements closed to resonance longitudinal surface plasmon peak in gold nanorods (Au NRs). Saturable absorption manifests itself at low excitation (laser irradiances $< \sim 7.0 \text{ GW/cm}^2$), while reverse saturable absorption dominates at higher excitation. Both the nonlinear processes are found to increase with the aspect ratio of Au NRs. Based on the discrete dipole approximation, qualitative explanations are presented for the observed nonlinear behavior. While common behavior in metallic quantum dots or other shapes of metallic nanomaterials was not the significant in our observation.

Keywords: Unique character, Aspect ratio, Gold nanorod, Optical nonlinearity.

LETTERS

Frontier works in nanoscience and nanotechnology currently have paid various multidisciplinary investigations particularly in conjunction with the nonlinear optical (NLO) behaviors in metal nanorods due to their wide impacts in many integrated applications including in advanced photonics devices [1-5]. The normal behaviors of NLO processes in metal nanorods have been well known to be significantly much more improvements in many physical properties than those in the bulk or nanoparticles. Furthermore, recent research

works related to the strong enhancement of emission from gold nanorods (Au NRs) near their surface plasmon resonance (SPR) have made Au NRs promising for many applications in nanotechnology [6-8]. Surface plasmon consists of electromagnetic waves that oscillate collectively at a metal/dielectric interface. Because of its capability to localize and guide light in sub-wavelength metallic nanostructures, surface-plasmon-based photonics or plasmonics, offers an opportunity to merge photonics and electronics on nanoscale dimensions. Moreover, NLO effects, including saturable absorption and reverse saturable absorption, are also enhanced considerably due to the local-field enhancement occurring at the SPR as a result of large optical

polarization associated with the collective electron oscillations. As such, there have been many reports on the interesting **NLO** properties of metal nanoparticles/nanowires that give immense enthusiasm for their applications such as optical limiters, filters, waveguides, lenses, polarizers, sensor protection, biological imaging, medicine, and nanoprobe [9-13].

In this letter, we report a unique character of nonlinear optical phenomena changing due to saturable absorption (**SA**), and reverse saturable absorption (**RSA**) which are dependence on both the aspect ratio of Au NRs and femtosecond laser light intensity at ~ 700 nm, 800 nm and 880 nm wavelengths, respectively. Our investigation into the aspect-ratio-dependent **NLO** properties of Au NRs was carried out in such above mentioned wavelengths with the aim of approaching to their longitudinal peak mode of **SPR**.

Figure 1. Typical TEM images of Au NRs with aspect ratios of 2.7 (a) and 3.8 (b).

The details of preparing Au NRs were reported elsewhere [12]. According to the transmission electron microscopic (TEM) images, as displayed in **Fig. 1**, we obtained the three samples of Au NRs with the aspect ratio as follows: 2.7, 3.8, and 3.95, respectively. The absorption spectra of the three samples of Au NRs dispersed in water were measured with an ultraviolet-visible spectrophotometer (UV-1700 Shimadzu). As shown in **Fig. 2(a)**, it is evident that there are two SPR peaks. The first and small SPR peak for all the three samples is located almost at the same wavelength of 520 nm, and it is due to the transverse mode perpendicular to the Au NRs, (and the average width of all Au NRs has approximately the same size); and the second and large **SPR** peak are located at different wavelengths of 675, 800, and 885 nm, and these **SPR** peaks are due to the longitudinal mode of SPR with the peak position depending on the length of Au NRs.

It is well-known that the longitudinal surface resonance exhibits a larger redshift with a greater aspect ratio (the length divided by the width) of metal nanorods. To gain more insight into the spectra described above, we have carried out the theoretical calculation using the discrete dipole approximation (**DDA**) method. The **DDA** method has been regarded as one of the most powerful and flexible electrodynamic methods for computing the extinction coefficient and optical scattering of metallic nanostructures with an arbitrary geometry [14,15]. In our calculation, we have adopted the **DDA** code developed by Draine and Flatau [1,16]. We first characterize the case with fixed orientation where the propagation direction of the incident light is assumed to be perpendicular to the axis of symmetry (long axis) the nanorod; and then averaged all the directions by considering the random distribution of Au NRs in our experiments. The nanorod is considered to have a geometry being a cylinder capped with two hemispheres. The calculations are carried out for varying aspect ratios of the nanorods. The theoretical results are shown in **Fig. 2(b)**, which is qualitatively

agreeable to the data in **Fig. 2(a)**. The calculated longitudinal modes have a narrower bandwidth and are red-shifted, compared to the experimental data. The difference may be attributed to the fact there is a finite size dispersion of Au NRs used in the experiment. It is particularly larger for Au NRs of smaller aspect ratios which have relative larger dispersions in the length.

Figure 2. (a) Measured absorbance and (b) theoretical spectra of Au NRs in water with different aspect ratios. The measured absorbance spectra are normalized to the peak of the longitudinal SPR. The inset in (b) zooms into the weak transverse SPR at ~520 nm.

The longitudinal-SPR NLO properties of Au NRs with the aspect ratio of 3.8 has been studied in detail and reported previously [12]. Here, we focus our attention to the NLO measurements with femtosecond Z-scans at

laser wavelengths (~700 nm, 800 nm and 880 nm) near/at the peak positions (675 nm, 800 nm and 885 nm) of longitudinal SPR for the three samples, respectively. To minimize accumulative thermal effects, we employed 220-fs laser pulses at 1-kHz repetition rate. The laser pulses were generated by a modelocked Ti: Sapphire laser (Quantronix, IMRA), which seeded a Ti:Sapphire regenerative amplifier (Quantronix, Titan). The wavelengths were tunable as the laser pulses passed through an optical parametric amplifier (Quantronix, TOPAS). The laser pulses were focused onto a 1-mm-thick quartz cuvette which contained the Au NR solution with a minimum beam waist of 10 μ m. By adding water to the Au NR solution, the linear transmittance of all the solutions was adjusted to be ~70% at the laser wavelengths, which kept the same value for the linear absorption coefficient. The incident and transmitted laser powers were monitored as the cuvette was scanned along the Z direction or the propagation direction of the laser pulses. **Figure 3(a)** shows typical open-aperture Z-scans for all the Au NR samples performed with the same irradiance of 1.8 GW/cm², demonstrating negative signs for the absorptive nonlinearities. We attribute this negativity to saturable absorption (SA), or the bleaching of the ground-state plasmon at the longitudinal mode of SPR due to the excitation of the electrons in Au NRs.

As the excitation irradiance is increased further beyond 7.0 GW/cm², as shown in **Fig. 3(b)**, the reverse saturable absorption (RSA) happens due to excited-state absorption (or free-carrier absorption) and nonlinear scattering. To quantify both SA and RSA, we employ the following expression for the entire absorption coefficient of Au NRs in solution:

$$\alpha(I) = \frac{\alpha_0}{\sqrt{1 + I/I_s}} + \beta I, \quad (1)$$

where α_0 is the linear absorption coefficient, I is the laser intensity, I_s is the saturation intensity, and β is the

nonlinear absorption coefficient which includes excited-state absorption and nonlinear scattering. In the denominator of the second term on the left side of **Eqn. (1)**, the square root is used to reflect the inhomogeneous nature of our system since the sizes of Au NRs are not uniform. By applying **Eqn. (1)** to Z-scan theory, we obtain Z-scan simulations. From the best fittings, we unambiguously extract the two parameters as I_s can be determined at lower irradiances and subsequently β is obtained at higher irradiance. The extracted values are as follows: $I_s = 0.08, 0.085, 0.07 \text{ GW/cm}^2$; and $\beta = 0.1, 0.15, 0.58 \text{ cm/GW}$ for the three samples of aspect ratios: 2.7, 3.8 and 3.95, respectively.

Figure 3. Open-aperture Z-scans (symbols) measured at (a) $I = 1.8 \text{ GW/cm}^2$ and (b) $I = 8.5 \text{ GW/cm}^2$ of Au NRs with different aspect ratios of 2.7, 3.8, and 3.95, respectively. The solid curves are the Z-scan simulations by **Eqn. (1)** in the text.

Within the experimental errors, the values of the measured saturation intensity are independent of the aspect ratio. If one expands the first term on the left side of **Eqn. (1)**, one can approximate the third-order nonlinear absorption coefficient to $\alpha_2 \approx -\alpha_0/2I_s$. Since I_s is independent of the aspect ratio, then α_2 is directly determined by $|\alpha_0|$, which is increased with the aspect ratio, as shown in **Fig. 2(b)** by the qualitative calculation based on the **DDA** method. As such, one concludes that α_2 is increased with the aspect ratio. The aspect-ratio dependence of β should be anticipated as well since it is induced from light scattering to a large extent. The **DDA** calculation predicts that the light scattering effect gets stronger as the length of Au NRs increases. As such, the magnitude of nonlinear scattering becomes greater as well.

Finally, based on our scientific measurements and theoretical findings mentioned in the former paragraphs, a remarkable different between normal behaviors and unique character of **NLO** processes in metal nanorods is not solely on more improvements in physical properties, but also on its evolution nonlinear characters in keep changing as high intensity fs laser changes during light-nm scale matter interactions with them especially on their longitudinal **SPR** with larger number of surface plasmon electrons than that in their transversal **SPR** mostly associated with their diameter of rods.

In conclusion, we have observed the evolution nonlinear characters with aspect-ratio dependence of **NLO** properties in Au NRs with femtosecond Z-scans at/near longitudinal **SPR**. The nonlinear absorption properties in Au NRs are found to be dependent on excitation irradiance. Saturable absorption occurs at low laser irradiances ($< \sim 7.0 \text{ GW/cm}^2$) and its magnitude increases as the aspect ratio increases. Reverse saturable absorption dominates the higher irradiance regime, and it is dependent on the aspect ratio in a similar fashion. The mechanisms responsible for such aspect-ratio dependence are discussed under the discrete dipole

approximation. While the evolution nonlinear optical characters were observed by changing the fs laser intensity as well as its tunable wavelengths closed to the longitudinal SPR peak.

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