Change of optical nonlinear absorption in gold nanoparticles

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The optical nonlinear absorption of the gold nanoparticles protected by C60 derivative was investigated by using open aperture Z-scan experiments with nanosecond pulse laser at wavelength of 532 nm. The shift from saturable absorption (SA) to reverse saturable absorption (RSA) was observed with increasing input pump intensities. The SA was ascribed to the bleaching of ground state plasmon band and the RSA was ascribed to excited state absorption of material. The competition of the two different effects caused the observed switching behavior in gold nanoparticles.

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1. Introduction

Nanostructured materials have unique physical and chemical properties different largely from those of the corresponding single molecules and bulk materials [1]. In recent year, metal nanoparticles, in particular noble metals, have attracted substantial attention, due to their possible applications in optoelectronics and their anticipated versatility in providing a deeper understanding of sized-sealed structure-function relationships [2].

For example, intensive studies were pursued in the optical limiting (OL) of silver and gold nanoparticles [2-11] because they both show a surface plasmon resonance (SPR) band in the visible region of the electromagnetic spectrum. Wenfang Sun [2] investigated the OL of a covalently bonded gold nanoparticle/polylysine hybrid material. Lakshminarayana Polavarapu [3] investigated the OL properties of oleylamine-capped gold nanoparticles for both femtosecond and nanosecond laser pulses. Reji Philip [4] and coworkers investigated the OL and optical nonlinearity of monolayer-protected gold, silver and gold-silver alloy nanoclusters with size of 3-4nm. They found that alloy nanoclusters were less efficient in OL than their monometal counterparts. Ya-Ping Sun [5] and coworkers investigated the OL of silver-containing metal-halide clusters and nanosols. They found that the OL of the materials was even stronger than those of the benchmark materials fullerenes and metallophthalocyanine. Chan Zheng [6] investigated the OL of Graphene oxide–noble metal (Au, Pt, and Pd) nanoparticle composites.

In order to obtain the materials with stronger OL, we also have previously synthesized silver and gold nanoparticles protected by C60 derivatives and studied their optical nonlinearities and OL behavior using 8ns laser pulses at 532nm [7-10]. We found that they both can show enhanced OL even better than well-reported optical limiter, C60 in toluene, and they are potential candidates of optical limiters.

However, because the laser pulse used in our previous experiments is relatively stronger, only RSA and OL have been observed in those experiments [7, 8]. Recently, we conduct open aperture Z-scan measurement in the gold nanoparticles again with relatively weak laser pulse. To our surprise, the gold nanoparticle is found to exhibit not only RSA but also SA depending on pump intensity. Identification of this intensity is important when we consider OL applications, since such applications require a relatively low threshold for the limiter. The dynamics responsible for the peculiar behavior is discussed and analyzed theoretically.

2. Samples and experiments

The sample investigated in our experiments is gold nanoparticle stabilized by C60 fullerene-substituted oligopyridines. It was prepared through the reduction of $[AuCl]^-$ by aqueous sodium borohyclried. The details about synthesis have been reported in ref. [7]. For the sake of convenience, it is denoted as C60TPY-Au. The structure of ligand C60TPY is shown in Fig. 1. As shown in Fig. 2, the absorption spectra of C60TPY-Au, exhibits a weak SPR absorption band ranging from 500nm to 600nm, which is ascribed to a collection oscillation of conduction electrons in response to optical excitation. The average

size of C60TPY-Au was estimated by transmission electron microscopy (TEM) to be of the order of 5-15 nm.

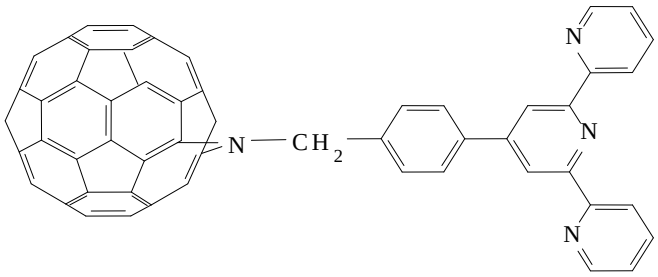

Fig. 1. Molecular structure of the ligand C60TPY

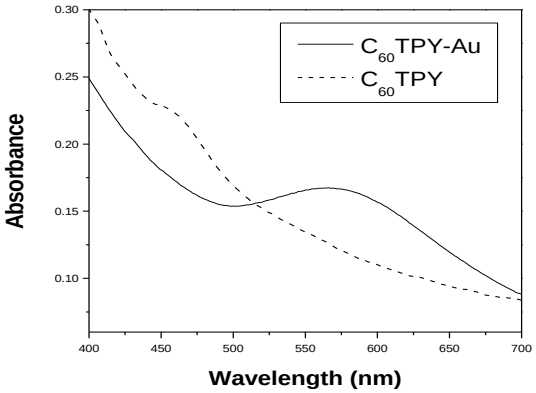

Fig. 2. Linear absorption spectra of C60TPY-Au and C60TPY

The laser used is generated by a frequency-double, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser system, operating at the repetition rate of 1Hz and producing 8ns laser pulses at 532nm wavelength. The laser pulses are spatially and temporally Gaussian. The open aperture Z-scan experiments were conducted using a typical set up [17]. In Z-scan experiments, a lens with a focal length of 308mm was used to focus laser beam. The focal spot size was measured to be 110um in diameter using CCD. C60TPY-Auwas dissolved in chloroform and filled with a quartz cuvette with a 2mm thickness. The linear transmission of the sample is 75% for 532nm wavelength. Sample was fixed on a computer-controlled translation stage, so that it could be accurately moved through the focal region of the laser beam over a length. At each z position, the sample can see different laser intensity, and the position dependent transmission is measured by using two energy detectors (Rjp-735 energy probes, Laser precision) to simultaneously monitor incident and transmitted laser pulses, respectively. The detected signals were acquired, stored and processed by a computer.

3. Results and discussions

The open aperture Z-scan measurements on gold nanoparticles are shown in Fig. 3(a-d). It can be found that gold nanoparticles exhibit different nonlinear absorptions depending on excitation intensities. At relatively low excitation intensity of $1.2\times10^{11}W/m^2$ or below, as shown in Fig. 3(a), the sample displays SA behavior. As the sample moves towards beam focus, the pump intensity increases, and the transmission increases correspondingly, indicating an optically induced transparency in gold nannoparticles.

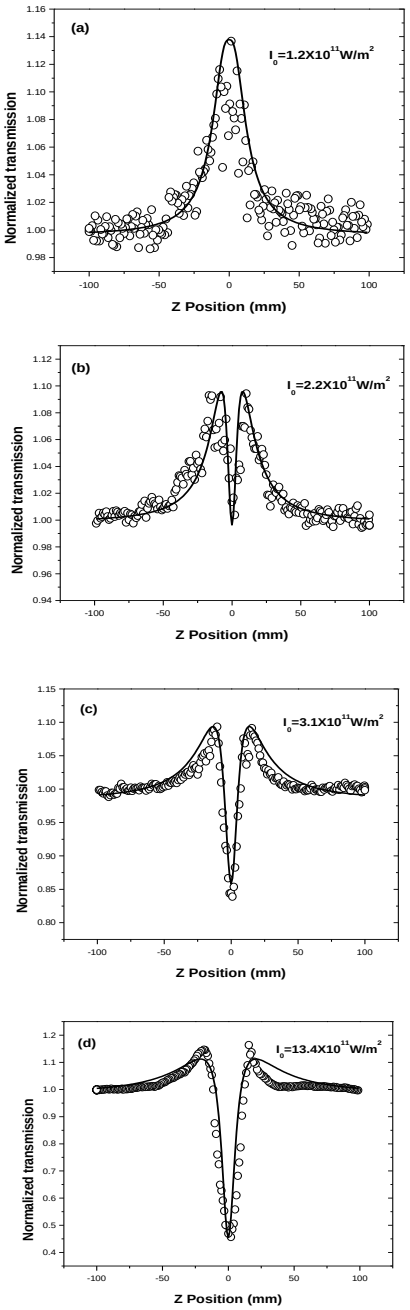

Fig. 3. Normalized transmission as a function of sample (C60TPY-Au) position for open aperture Z-scan at different intensities. Solid lines show theoretical fit generated using Eqs. (1-4). I_0 is on-axis peak intensity at focus

But at high intensities of $2.2\times10^{11}W/m^2$, $3.1\times10^{11}W/m^2$ and $13.4\times10^{11}W/m^2$ respectively, gold nanoparticles exhibit an additional RSA effects. Namely, when the sample approaches focal point, nonlinear absorption transforms from SA into RSA. To estimate the role of C60TPY, open aperture Z-scan experiment was conducted in C60TPY chloroform with low laser intensity, but only RSA effect was found. This indicates that the transition of nonlinear absorption results from gold nanoparticles.

Similar switching behaviors have also been previously observed in other gold [12-13], silver [4] and platinum [15,16] nanoparticles. The mechanism can be visualized as follows. The switching from SA to RSA was a consequence of competition between ground state plasmon bleaching and induced absorption [12-16]. As the absorption spectra of C60TPY-Au nanoparticles exhibits a SPR absorption band ranging from 500nm to 600nm, excitation at 532nm will prepare the system onto the excited state. When the irradiance is moderate, majority of the gold nanoaprticles are pumped onto the excited state, causing a smaller population of the ground state. This is called ground state bleaching of plasmon band. Thus more light is transmitted and the transmittance becomes higher than unity in open-aperture Z-scan measurement, resulting in SA. However, under higher laser intensities, when sample is moved closer to focal point, induced nonlinear absorption will occur and become stronger than SA. Less light is transmitted and the transmittance falls drastically, resulting in RSA and limiting. Thus a "hump" in open-aperture Z-scan curves is observed. The RSA in metal nanoparticles were usually believed due to the free carrier absorption [14]. As the gold nanoparticles in our experiment are protected by C60TPY, we believe that the excited state absorption of C60TPY also contributes to the RSA.

When there is only two-photon absorption in open-aperture Z-scan experiment, the normalized transmittance is [17]:

$$T(z)=\sum_{m=0}^{\infty}\frac{[\frac{-\beta I_0 L_{eff}}{1+z^2/z_0^2}]^m}{(m+1)^{3/2}} \tag{1}$$

where L_{eff} is the effective interaction length defined by $L_{eff}=(1-e^{-\alpha_0 L})/\alpha_0$, z is the longitudinal displacement of the sample from the focus (z=0), α is the nonlinear absorption coefficient, I_0 is the on-axis peak intensity at the focus (z=0), α_0 is the linear absorption coefficient, L is the sample length, z_0 is the Rayleigh diffraction length.

But when there is a changeover in the sign of the nonlinear absorption, we can phenomenologically define a nonlinear absorption coefficient by combining a saturation absorption coefficient and two-photon absorption (TPA) coefficient [15]:

$$\alpha(I)=\alpha_0\frac{1}{1+I/I_s}+\beta I \tag{2}$$

Where the first term describes negative nonlinear absorption such as SA, and the second one describes positive nonlinear absorption such as RSA and/or two-photon absorption. α_0 is linear absorption coefficient which is $143.8m^{-1}$ at 532nm in our experiment. I and I_s are laser radiation intensity and saturation intensity, respectively. β is positive nonlinear absorption coefficient. We know that I can be expressed as:

$$I=\frac{I_0}{1+z^2/z_0^2} \tag{3}$$

So Eq. (2) can be denoted further as:

$$\alpha(I_0)=\frac{\alpha_0}{1+\frac{I_0}{(1+z^2/z_0^2)I_s}}+\frac{\beta I_0}{1+z^2/z_0^2} \tag{4}$$

Thus, theoretical fit to the experimental data could be conducted by replacing $\beta I/(1+z^2/z_0^2)$ in Eq. (1) by Eq. (4). Using $I_s=1.3\times10^{10}W/m^2$ and $\beta=3.5\times10^{-10}m/W$, reasonable fit is obtained. Solid lines in Fig. 3 (a, b, c, d) show the theoretical curves for different intensities. We can find that the theoretical fitting is in good agreement with the experimental results, which indicates the model used is reasonable. But we can also find there is still a little difference between theoretical fitting and experimental data in Fig. 3 (d). We believe this may be due to nonlinear scattering at high intensity.

4. Conclusion

In summary, the changeover from SA to RSA was investigated at the wavelength of 532nm in gold nanoparticles protected by C60 derivative. It was found that the sample shows SA for lower intensities, while RSA for higher intensities. The novel phenomenon was analyzed theoretically. The saturation intensity and nonlinear absorption coefficient were obtained to be $I_s=1.3\times10^{10}W/m^2$ and $\beta=3.5\times10^{-10}m/W$, respectively.

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