Paradoxical Combination of Saturable Absorption and Reverse-Saturable Absorption in Plasmon Semiconductor Nanocrystals

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Supporting Information

1. Experiment section

Synthesis of Al-doped ZnO nanocrystals (AZO NCs)

The Al-doped ZnO nanocrystals were prepared by using zinc salts with the dopant ions in basic solution and the details is shown in our previous work.[1] In short, Zinc acetate dehydrate (8.714g, $Zn(CH_3COO)\cdot 2H_2O$, 99.99%, Aladdin), aluminum hydroxide (0.958g, $Al(OH)_3$, 99.9%, Aladdin), sodium hydroxide (NaOH, Aladdin) and distilled water (13 ml) were firstly dissolved in 80 ml diethylene glycol (DEG). Here, the Al dopant was adjusted to be 1wt% (or 3at%) to make sure that the start LSPR wavelength is less than 800 nm (the femtoseconds laser wavelength). The mixture was then heated up to 189 ^{o}C by oil-bath heating. After centrifuging and washing several times, the obtained nanocrystals were then dried in vaccum for next measurements. The Al-doped ZnO nanocrystals was dispersed into alcohol by ultrasonic oscillation and then spin-coated onto a 0.5 cm thick high-purity quartz slide for 10 times for characterization.

Characterization of Al-doped ZnO nanocrystals

A confocal microscopy system (Renishaw inVia, Gloucestershire, UK) operated at 532 nm excitation source was used to record Raman signal. A Bruker diffractometer with Cu Kα_1 radiation (λ=1.5418 Å) was used to record the XRD pattern. A Perkin-Elmer Lambda-900 UV-Vis-NIR spectrophotometer (Perkin Elmer, Waltham, MA) was used to measure the linear optical absorption. An empty quartz slide was used to be a reference. The transmission electron microscope (TEM) images were recorded by a JEOL-2100F at 200 kV. Elemental analysis was measured by induced coupled plasma atomic emission spectroscopy (ICP-AES) with a Varian 720/730 Series spectrometer.

Z-scan

Optical nonlinearities at 800 nm and 1550 nm were performed by a well-developed open-aperture Z-scan technique. The detailed description is shown in our previous work.[2, 3] In short, a commercial Ti:sapphire regenerative amplifier system (800 nm, 1 kHz, 130 fs) was employed to be the laser source. The wavelength is tuned by an optical parametric amplifier (OPA) from 800 nm to 1550 nm. The 0.5 mm thick high-purity quartz slide coated with the synthesized Al-doped ZnO nanocrystals was settled on a linear translation stage, which can move near the focus to imitate the change of the femtosecond laser intensity.

Pulse generation

The laser cavity is based on 2 m-long erbium-doped gain fiber (EDF). Another single mode fiber (SMF)-28e was used as the pigtails of the corresponding components. A commercial 980 nm laser was used to excite the gain fiber through a 980/1550 nm wavelength division multiplexer (WDM). The cavity birefringence was adjusted by employing a polarization controller (PC). In order to make sure the single-direction operation, a polarization-independent optical isolator was constructed into the cavity. A 90:10 fiber coupler was adopted to output the laser. The AZO/PVA composite film was embedded between two fiber connectors and integrated into the laser cavity as saturable absorber for Q-switching operation. More details is shown in other article.[2]

2. Calculation of nonlinear absorption coefficient

For three-order nonlinearity process, the total absorption coefficient can be expressed as:

$$\alpha(I) = \alpha_0 + \beta I \qquad \text{(S1)}$$

where α_0 is the linear absorption coefficient and β is three-order nonlinear absorption coefficient. The open-aperture Z-scan normalized transmittance can be expressed as:[4]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}},\ q_0(z,0) = \frac{\beta L_{\mathrm{eff}} I_0}{(1 + z^2/z_0^2)} \qquad \text{(S2)}$$

where I_0 is the laser intensity at the focal plane; z is the sample position; $z_0=\pi\omega_0^2/\lambda$ presents the Rayleigh range, ω_0 presents the minimum beam waist at the focal plane (z=0), λ presents the laser free-space wavelength; $L_{\mathrm{eff}}=(1-\exp(-\alpha_0 L))/\alpha_0$ is the effective length for three-order nonlinearity process; L is the sample length.

In three photon absorption (fifth-order nonlinearity) process, the total absorption coefficient can be described by:

$$\alpha(I)=\alpha_0+\gamma I^2 \qquad \text{(S3)}$$

where γ is three photon absorption coefficient. The open-aperture Z-scan normalized transmittance can be deduced as:[5]

$$T(z) = \frac{1}{\pi^{1/2} p_0} \int_{-\infty}^{\infty} \ln\left\{\left[1 + p_0^2 \exp(-2x^2)\right]^{1/2} + p_0 \exp(-x^2)\right\} dx \qquad \text{(S4)}$$

where $p_0 = \left(\frac{2\gamma I_0^2 L'_{\mathrm{eff}}}{(1 + z^2/z_0^2)^2}\right)^{1/2}$, $L'_{\mathrm{eff}}=[1-\exp(-2\alpha_0 L)]/(2\alpha_0)$ is the effective length for three photon absorption process.

In the three-order nonlinearity and fifth-order nonlinearity (three photon absorption) process, the total absorption can be expressed as:

$\alpha(I)=\alpha_0+\beta I+\gamma I^2$ (S5)

The polynomial solution of the normalized transmittance as a function of the sample position $x=z/z_0$ is deduced as:

$$T(x,t) = \exp(\alpha_0 L)\left[1 + \sum_{m=1}^{\infty} (-GL)^m q_m(\rho)\right] \quad \text{(S6)}$$

here, $\rho=I_0\exp(-t^2/\tau^2)/[I_s(1+x^2)]$, τ is the half-width at e^{-1} of the maximum for the pulse duration; $G = \alpha_0 + \beta I_s + \gamma I_s^2$, I_s is the saturable intensity. The first term of $q_m(\rho)$ is considered and the $q_1(\rho)$ is given as:[6]

$$q_1(\rho) = \left[(\alpha_0 + \beta I - \gamma I_s^2)\rho + \frac{\gamma I_s^2 \rho^2}{2} + (\gamma I_s^2 - \beta I_s)\ln(1+\rho)\right]/(\alpha_0 + \beta I_s + \gamma I_s^2) \quad \text{(S7).}$$

All the parameters are defined as the above. Hence, the open-aperture Z-scan normalized transmittance can be deduced as:[6]

$$T(x) = \frac{1}{\sqrt{\pi}\tau}\int_{-\infty}^{\infty} \mathrm{T}(x,t)\exp(-t^2/\tau^2)dt \quad \text{(S8).}$$

3. Additional Figures

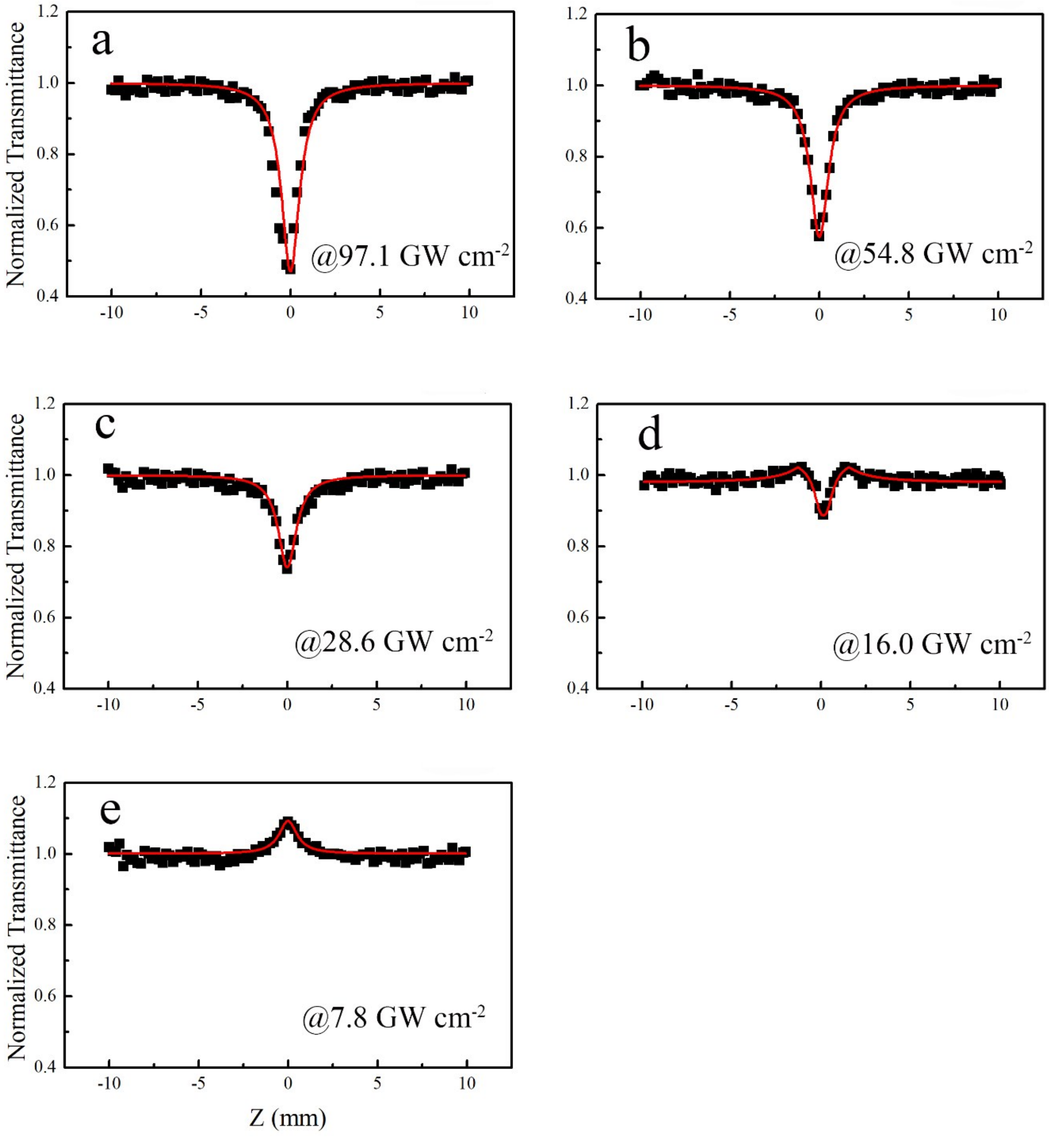

Fig. S1. Open Z-scan results (black square) and fitting curves (red line) of the AZO/Quartz film measured by decreasing the pump laser intensity.

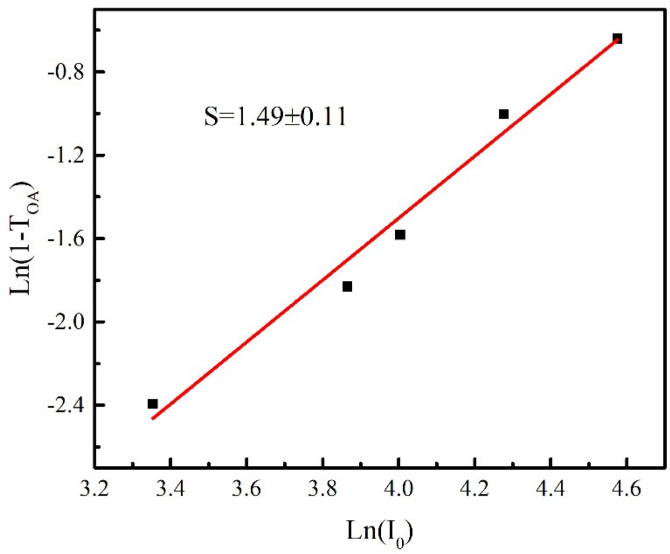

Fig. S2. The relationship between Ln(1-T*OA*) and Ln(I_0) shows the slope is about 1.49, which indicates three-photon absorption behavior under higher irradiation intensity range.

References:

1. X. Tian, H. Luo, R. Wei, M. Liu, Z. Yang, Z. Luo, H. Zhu, J. Li and J. Qiu, *Nanoscale*, 2019, **11**, 13988-13995.
2. R. Wei, H. Zhang, X. Tian, T. Qiao, Z. Hu, Z. Chen, X. He, Y. Yu and J. Qiu, *Nanoscale*, 2016, **8**, 7704-7710.
3. X. Tian, H. Luo, R. Wei, C. Zhu, Q. Guo, D. Yang, F. Wang, J. Li and J. Qiu, *Adv. Mater.*, 2018, **30**, 1801021.
4. M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. V. Stryland, *IEEE J. Quant. Electron.*, 1990, **26**, 760-769.
5. J. He, Y. Qu, H. Li, J. Mi and W. Ji, *Opt. Express*, 2005, **13**, 9235-9247.
6. J. Wang, B. Gu, X.-W. Ni and H.-T. Wang, *Opt. Laser Technol.*, 2012, **44**, 390-393.