Phenothiazine-Silver Hybrid System Exhibiting Switching and Photo-induced Enhancement in Nonlinear Optical Absorption

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Supplementary Information (SI)

SI- I: Density calculation of Silver Nanoparticles[1-3]

Density (ρ) : 10.49g/cm^3

Specific heat of evaporation (Ω)/ Latent heat of vaporization (L_v) : 255 kJ/mol = 2.37× 10^3J/g

Absorption coefficient (α) : 8.35 × 10^5 cm^{-1} (for 532 nm)

Thermal conductivity (k): 430 W/(m K)

Specific heat (c_p): 235 J/ (Kg K)

Heat diffusion coefficient/thermal diffusivity $(D) = \frac{k}{c_1}$ = 1.74x10^{-4}m^2/S ($c_1 = c_p\rho$)

Ablation threshold (F_{th}) ≈ $\boldsymbol{7ns}$ for the nanosecond system and $\boldsymbol{\lambda}$ = 532 nm

$F_{th} = \rho\Omega D^{1/2}\tau_p^{1/2} = 2.27 J/cm^2$

Fluence in the case of a nanosecond laser (F_a) = $41.5 J/cm^2$ (Input energy = 20 mJ)

Ablation depth (L) $= \alpha^{-1} ln(\frac{F_a}{F_{th}}) = 2.1 \times 10^{-5} cm$

Quantity of Ablated Material (V) $= \frac{1}{3}\pi r^2 L = 3.18 \times 10^{-14} m^3/pulse$

Mass of particles ablated / pulse $= V \times \rho = 3.33 \times 10^{-10} Kg/pulse$

Total number of pulses in 20 minutes = $20 \times 60 \times 10$

Amount of Ag nanoparticles formed in 20 minutes $= 3.99\mu g$

References:

(1) Chicbkov, B.N.; Momma, C.; Nolte, S; yon Alvensleben, F.; Tiinnermann, A. Appl. Phys. A , **1996**, *115*, 109–115.

(2) Gamaly, E. G.; Rode, A. V.; Luther-Davies, B.; Tikhonchuk, V. T. Ablation of Solids by Femtosecond Lasers: Ablation Mechanism and Ablation Thresholds for Metals and Dielectrics. *Phys. Plasmas* **2002**, *9* (3), 949.

(3) Smijesh, N.; Philip, R. Emission Dynamics of an Expanding Ultrafast-Laser Produced Zn Plasma under Different Ambient Pressures. *J. Appl. Phys.* **2013**, *114* (9), 1–5.

SI-2: FTIR Analysis

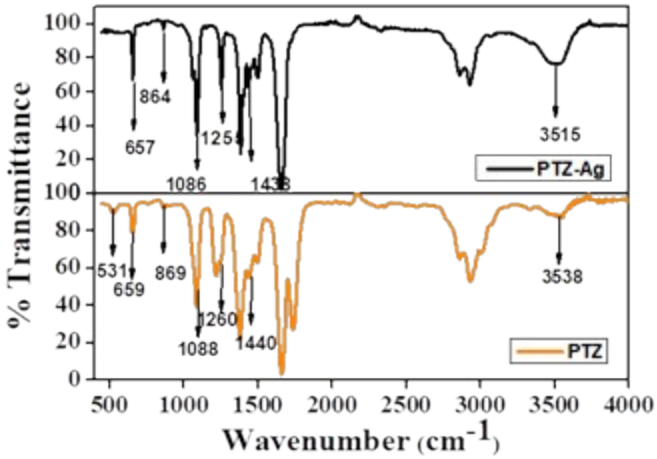

Fig.SI-1: FTIR spectra of PTZ, PTZ-Ag hybrid system

The spectrum was recorded using JASCO FT / IR-4700 in ATR mode. Peaks were assigned according to the literatures[1,2]. The peak at 659 cm^{-1} is due to angle bending δs (C–N–C) and δs(N–H), and peak at 869 cm^{-1} is accredited to angle bending of δs (N–H) and δs (C–C–C)). The peak at1260 cm^{-1} is owing to symmetric stretching of υs(C-N-C) angle bending of (C-H)).

The N-H stretching frequency of PTZ[3] is located at 3538 cm^{-1} and these peaks are down shifted to 657 cm^{-1}, 864 cm^{-1}, 1255 cm^{-1} and 3515 cm^{-1}respectively.

References

1. M. Alcolea Palafox, M. Gil, J. L.Nunez, G. Tardajos, *Int. J. Quantum Chem.*, 2002, **89**, 147–17.

2. A. Kumar, S. Mandal, P.R. Selvakannan, R. Pasricha, A.B. Mandale, and M. Sastry, s. *Langmuir***2003**, *19* (15), 6277–6282.

3. D. Pan and D. L. Phillips *J. Phys. Chem. A* 1999, 103, 4737-4743

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SI-3: SERS Enhancement factor calculation

$$EF = \left(\frac{I_s}{I_R}\right) \times \left(\frac{N_R}{N_s}\right)$$

Where Is and I_R are the intensities of the Raman band of PTZ-Ag and PTZ. N_S and N_R are the number of PTZ molecules in surface enhanced Raman mode and normal Raman mode.

Excitation wavelength – 633 nm

Peak taken for enhancement factor calculation – 1030 cm^{-1}

$I_S/I_{R\ is}$ obtained as 4.3

N_R is obtained by the equation, $N_R = \rho N_A V / (M.W)$,

Where ρ density of PTZ, NA is Avogadro number and $M.W$, molecular weight of PTZ. V is the volume of the sample and is same as the product of laser spot area with depth. Hence N_R is estimated to be 3.4×10^9.

Spot size and depth of excitation source 100 x lenses – 1x1 micrometer

ρ is density of PTZ – 1.296 g/ mL

MW of PTZ – 199.27 g/ mol

1×10^{-6} molar solution of PTZ was taken for surface enhanced Raman analysis. Number of molecules over the laser spot area is calculated as $1.5x10^4$

EF = $9.7x10^5$ ~ $1x10^6$

Reference

1. K. Hasna, A. Antony, J. Puigdollers, K. R. Kumar and M. K. Jayaraj, Nano Res., 2016, 9, 3075–3083

SI -4: FTDT simulation at 418 nm

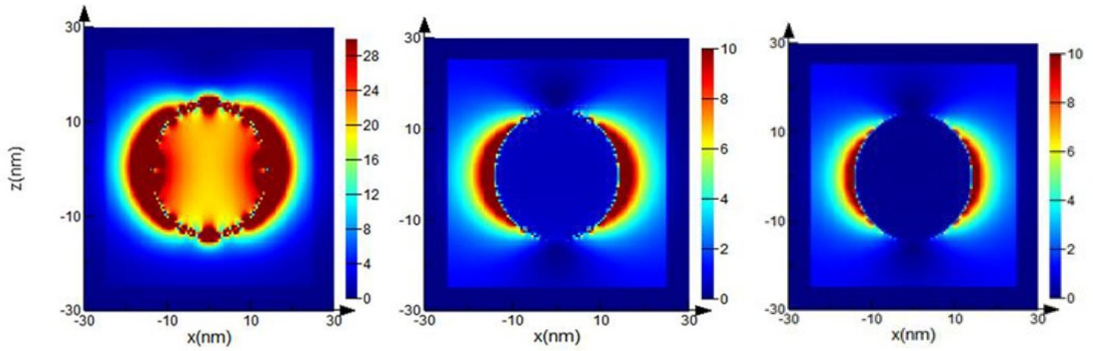

Fig. SI- 2: Normalized electric field intensity distribution of Ag NPs simulated in the XY plane at 418 nm, 532 nm and 633 nm

To investigate the effect field enhancement on near resonance, Plasmonic responses of the Ag NPs were analyzed using three dimensional finite difference time domain (FDTD) solution package (Lumerical solutions, Inc.). Its found that intensity of field enhancement is maximum, when the excitation wavelength is in resonance with SPR of NPs.

SI-5: Nonlinear absorption coefficient calculation

During the Z scan experiment, the spatial rate of change of intensity can be written as

$$\frac{dI}{dz} = -\alpha_0 I - \beta I^2 \qquad (1)$$

and total absorption coefficient

$$\alpha(I) = \alpha_0 + \beta I \tag{2}$$

Where α_0 Is the linear absorption coefficient and β is two photon absorption coefficient. SA has no role here, as it deals with genuine TPA.

When we consider saturable absorption alone, the net absorption coefficient α (I) contains saturable absorption part and TPA part won't be there.

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_s}} \tag{3}$$

When absorption became combinations of TPA and SA assisted ESA, the net absorption coefficient can be expressed as

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_s}} + \beta_{eff} I \tag{4}$$

And the propagation equation will be

$$\frac{dI}{dz} = -\left(\frac{\alpha_0}{1 + \frac{I}{I_s}} \right) I - \beta_{eff} I^2 \tag{5}$$

Where I and I_s are the laser intensity and saturation intensity. β_{eff} Is the effective TPA coefficient, which includes both TPA by PTZ and TPA and SA assisted excited state absorption (ESA) by Ag NPs

References:

1. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, *IEEE J. Quantum Electro*n.1990, 26 (4), 760–769.

2. V. Sreeramulu, K. K. Haldar, A. Patra, and D. N. Rao, "*J. Phys. Chem. C*, vol. 118, p. 303333, 2014

3. B. Anand, a Kaniyoor, S. S. S. Sai, R. Philip and S. Ramaprabhu, *J. Mater. Chem. C*, 2013, 1, 2773.