Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

Plasmonic core-shell nano-heterostructures with temperature-dependent optical nonlinearity

Chi Pang,[a] *Rang Li,*[a,b] *Ningning Dong,*[c] *Ziqi Li,*[a] *Jun Wang,*[c] *Feng Ren,*[d] *and Feng Chen**[a]

[a] School of Physics, State Key Laboratory of Crystal Materials and Key Laboratory of Particle Physics and Particle Irradiation (MOE), Shandong University, Jinan 250100, China. Email: drfchen@sdu.edu.cn.

[b] Collaborative Innovation Center of Light Manipulations and Applications, Shandong Normal University, Jinan 250358, China.

[c] Laboratory of Micro-Nano Optoelectronic Materials and Devices, Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China.

[d] Department of Physics, Center for Ion Beam Application and Center for Electron Microscopy, Wuhan University, Wuhan 430072, China.

Corresponding Author

* *Feng Chen: drfchen@sdu.edu.cn*

1. Ion distribution calculation

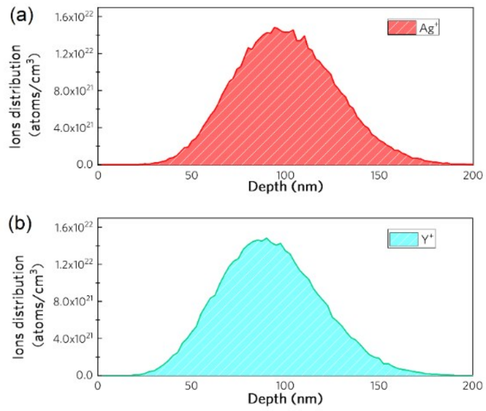

Fig. S1. SRIM simulation about Ag^+ and Y^+ ion distribution

Fig. S1 shows the calculated ion distribution of Ag^+ and Y^+ ions by SRIM. The implanted energies of Ag^+ and Y^+ ions are 200 keV and 150 keV, respectively. As shown, the maximum implanted depths of Ag^+ and Y^+ ion implantation are ~200 nm, and the implanted ions are mainly distributed at the depth of ~95 nm. According to the simulation results, it can be obtained that the implanted ions are distributed at similar region, which can promote the formation of core-shell nanostructures.

2. TEM characterizations

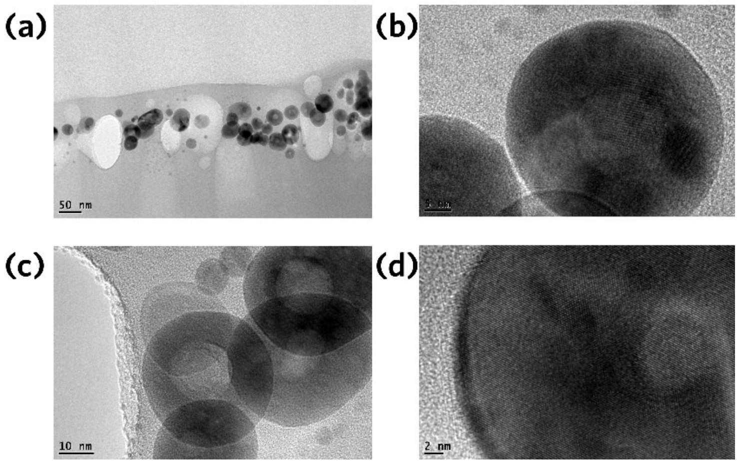

Fig. S2. TEM images of Y@Ag/AgY NPs

Fig. S2 shows the TEM images with wider range. As we can see, almost all the big NPs are core-shell structured. According to the statistics, the percent of the core-shell nanoparticles is ~ 80%.

3. Dependence of optical intensity, temperature, and nonlinearity of Ag NPs embedded SiO_2.

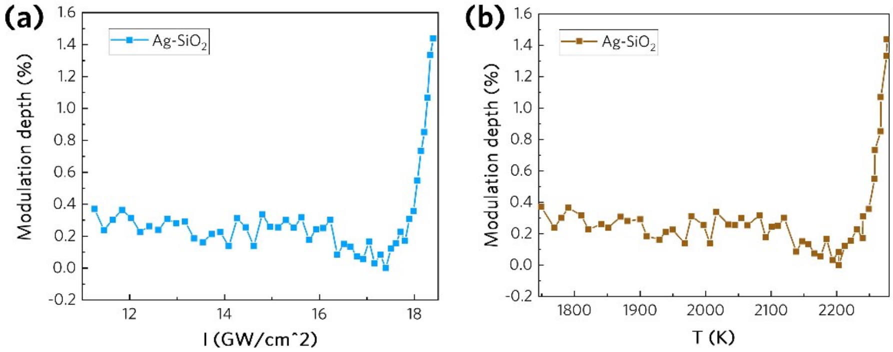

Fig.S3. (a) Dependence of optical intensity and modulation depth of Ag NPs embedded SiO_2. (b) Dependence of temperature and modulation depth of Ag NPs embedded SiO_2.

Based on the equations S1-S4, the dependence between laser intensity and value of Z laser intensity can be calculated.

$$I = E \cdot f / (\pi \cdot \omega(z)^2)$$ Eq. S1

$$\omega(z) = \omega_0 \cdot \sqrt{1 + \left(1 + \left(\frac{z}{z \cdot R}\right)\right)^2}$$ Eq. S2

$$z \cdot R = \frac{\pi \cdot \omega_0{}^2}{\lambda}$$ Eq. S3

$$\omega_0{}'^2 = \frac{\omega_0^2}{(1 - \frac{l}{F})^2 + \frac{1}{F^2}(\frac{\pi \omega_0^2}{\lambda})^2}$$ Eq. S4

4. Comparison of nonlinearity of Y@Ag/AgY NPs and Ag NPs.

The nonlinear optical responses of Y@Ag/AgY NPs and Ag NPs are compared with the cited references [S1]. The modulation depths are ~85% and ~25% for Y@Ag/AgY and Ag NPs NPs. In addition, the saturation intensities are 5.7 GW/cm^2 and 1.4 GW/cm^2 for Y@Ag/AgY and Ag NPs NPs, respectively.

5. Near-field distribution simulation.

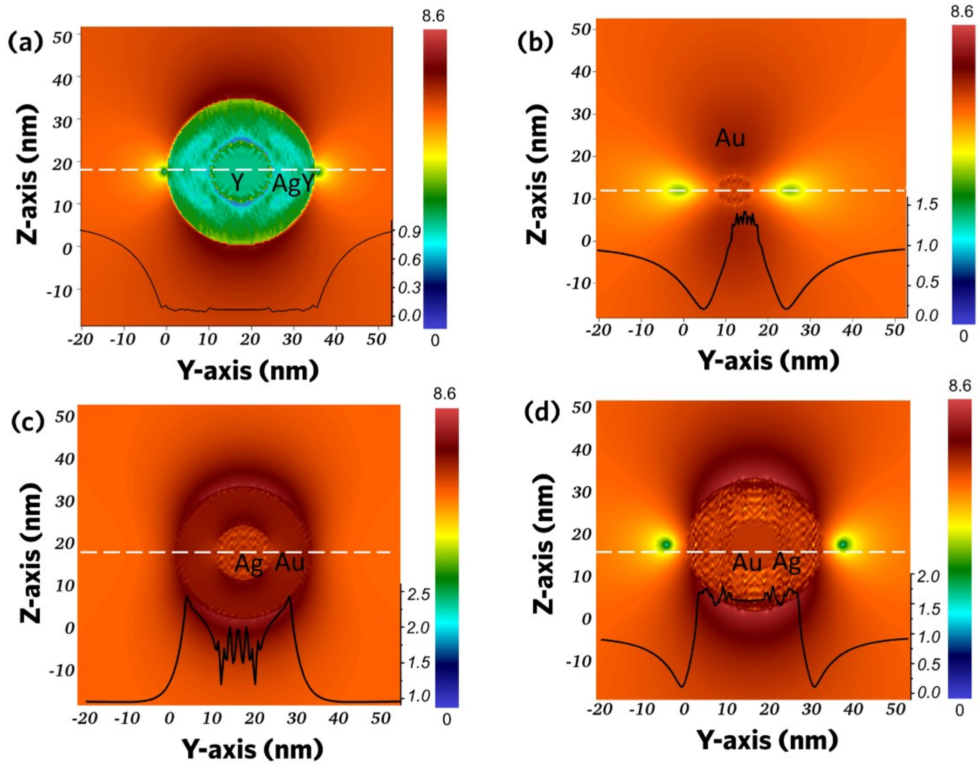

Fig. S4. Near-field distribution of (a) Y@AgY, (b) Au, (c) Ag@Au, and (d) Au@Ag core-shell NPs.

6. Calculation of near field intensity distribution by DDA

Based on the DDSCAT code, the near field intensity distribution is simulated by numerically solving Maxwell's equations using DDA. The number N of dipoles in target is set as many as 179309. In addition, the effective radiuses of core and shell in the software are calculated to be 7.5 nm and 17.5 nm by the equation:

$$a_{eff} = (3V / 4\pi)^{1/3} \quad \text{Eq. S5}$$

The error tolerance is as low as 1×10^{-5}, and the refractive index of SiO_2 is 1.46.

7. Temperature calculation

The size effect and incident optical intensity dependence on temperature can be calculated by Comsol Multiphysics® 5.5a. The modules used in the calculation are

CAD import module and wave optics module. A core-shell structure in substrate and Ag nanosphere embedded in substrate were constructed, respectively. According to the TEM measurement, the diameters of core and whole core-shell structure were set to be 15 nm and 35 nm, respectively. The diameter of Ag nanosphere was set to be 27 nm. The materials of substrate and core were set to be SiO_2 and Y, which can be directly selected in the build-in system material libraries. AgY was set as the material of shell and the refractive index of AgY was calculated by WASP® before being imported to the Comsol Multiphysics®. After meshing, setting parametric sweep is necessary to calculate the different optical intensities and different sizes of the core-shell structure. The optical intensity sweep range is from 0 GW/cm^2 to 50 GW/cm^2 with the interval of 2 GW/cm^2. The radius of core (r0) sweep range is from 3 nm to 12 nm with the interval of 1.2 nm. And the radius of core-shell structure is increased with the growth of core's size. The wavelength of incident laser is set to be 515 nm with the irradiation time of 25000 fs [50]. Finally, after investigation and calculation, the temperature under different optical intensities and sizes can be calculated.

References

[S1] R. A. Ganeev, A. I. Ryasnyansky, A. L. Stepanov and T. Usmanov, *Opt. Quant. Electron.* 2004, **36**, 949-960.

[S2] L. Stepanov, *Rev. Adv. Mater. Sci.* 2011, **27**, 115-145.

[S3] D. Ila, E. K. Williams, S. Sarkisov, C. C. Smith, D. B. Poker and D. K. Hensley, *Nucl. Instrum. Meth. B* 1998, **141**, 289-293.

[S4] B. Joseph, C. S. S. Sandeep, B. R. Sekhar, D. P. Mahapatra and R. Philip, *Nucl. Instrum. Meth. B* 2007, **265**, 631-636.

[S5] Y. H. Wang, S. J. Peng, J. D. Lu, R. W. Wang, Y. G. Cheng and Y. L. Mao, *Vacuum* 2008, **83**, 412-415.