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Electronic Supplementary Information

In-Situ Hydrosilane Reduction and Preparation of Gold Nanoparticles-Gel Glass Composites with Nonlinear Optical Properties

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1. Open aperture Z-scan measurement and analysis

The Z-scan experimental apparatus and following analysis were carried out according to literature¹. Our experimental apparatus employed an 8ns Nd: YAG laser operating at 532 nm and 1064 nm at a repetition rate of 10 Hz. The laser energy was adjusted to 30.5 μ J and 199 μ J at 532 nm and 1064 nm respectively. As shown in Fig. S1, the Gaussian laser was separated into two beams by a beam splitter. One beam was recorded by laser energy detector D1 as input energy. The other beam was focused by a lens, passed through the sample and was finally collected by laser energy detector D2. And the ratio D2/D1 was transmittance of the sample. The sample used for Z-scan should be transparent and uniform, and the thickness of the sample should be less than the Rayleigh length (Z_R) of the beam. The sample was placed on a precision linear translation stage, which the sample could move to any position along the direction of the laser propagation (Z axis), and we define the focus point as z=0. And Z-scan curve was obtained through normalized transmittance versus sample position.

For open aperture Z-scan measurement, the normalized transmittance is given by

$$T(z) = \frac{1}{\sqrt{\pi}q_0} \times \int_{-\infty}^{\infty} \ln\left[1 + q_0 e^{-\tau^2}\right] d\tau$$
 (1)

where $q_0 = \beta I_0 L_{eff} / (1 + z^2 / z_0^2)$ (2)

And $z_0 = k\omega_0^2/2$ is the diffraction length of the beam, $k = 2\pi/\lambda$ is the wave vector and λ is the wavelength. L_{eff} is the effective thickness of the sample, I_0 is the energy density at the focus (z=0).

$$L_{eff} = [1 - exp^{\pi 0}(-\alpha L)]/\alpha \quad (3)$$

Where α is the linear absorption coefficient and L is the thickness of sample. For $|q_0| < 1$, this transmittance can be expressed in terms of the peak irradiance in a summation form more suitable for numerical evaluation:

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m+1)^{3/2}} \approx 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2} \left(1 + z^2/z_0^2\right)} = 1 - [1 - T(z=0)]/(1 + z^2/z_0^2)$$
(4)

And β is the nonlinear absorption coefficient of the sample. Fitting the experimental data with equation (4), and β is obtained.



Fig. S1. The optical system for Z-scan measurement.

2. Optical limiting measurement

The experimental setup for optical limiting was according to literature². As shown in Fig. S2, the laser pulses were same as the Z-scan measurement. The input laser pulses energy was adjusted by a variable attenuator and split into two beams by a beam splitter. One beam was recorded by detector R as the reference of incident laser energy, and the other beam was focused by a lens and the transmitted through the sample and recorded by energy detector A. The ratio A/R represented the transmittance of the sample. The sample was placed at the focus. The input energy fluence could be changed by rotated the variable attenuator, and optical limiting curve obtained through normalized transmittance versus input energy fluence. For investigated nonlinear scatting of the sample, an aperture was placed before the detector A, and adjusted the aperture so that 50% of the light through.



Fig. S2. The optical system for optical limiting measurement.

3. Preparation of AuNPs suspension reduced by TPS

0.25mL 0.01 M HAuCl₄ distilled water solution, 5 mL distilled water, 5 mL ethanol, and 0.2 g PVP were added in a flask with magnetic stirring. Then 10 mg TPS was dissolved in 0.5 mL ethanol and quickly injected into the flask. The solution turned from yellow to wine red within 20 minutes, the TPS reduced AuNPs (TPSAu) were obtained.



Fig. S3. (a) TEM image of TPSAu and (b) size distribution histogram of TPSAu



Fig. S4. UV-vis spectrum of TPSAu



Fig. S5. Photographs of TPSAu (a) fresh prepared and (b) after one month

4. Preparation of AuNPs suspension reduced by poly(methylhydrosiloxane)

0.25mL 0.01 M HAuCl₄ distilled water solution, 5 mL distilled water, 5 mL ethanol, and 0.2 g PVP were added in a flask with magnetic stirring. Then 10 mg poly(methylhydrosiloxane) was dissolved in 0.5 mL ethanol and quickly injected into the flask. The solution turned from yellow to wine red within 20 minutes, the poly(methylhydrosiloxane) reduced AuNPs (PMHSAu) were obtained.



Fig. S6. (a) TEM image of PMHSAu and (b) size distribution histogram of PMHSAu



Fig. S7. UV-vis spectrum of PMHSAu



Fig. S8. Photographs of PMHSAu (a) fresh prepared and (b) after 7 days and (c)after

one month



Fig. S9. EDS spectrum of AuNPs-silane sol

Table S1. Element content of AuNPs-silane sol measured by EDS

Element	Weight present %	Atom present %
С	67.21	76.49
Ν	4.90	4.78
0	15.69	13.40
Si	10.73	5.22
Au	1.47	0.10



Fig. S10. The XPS spectra of (a) AuNPs-silane sol; (b) Au 4f region; (c) Si 2p region and (d) C 1s region.

- 1 M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, *IEEE J. Quantum Elect.*, 1990, **26**, 760-769.
- 2 G. Wang, and W. Sun, J. Phys. Chem. B, 2006, 110, 20901-20905.