Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Strong Optical Limiting Properties of Ormosil Gel Glasses Doped with Silver Nano-particles

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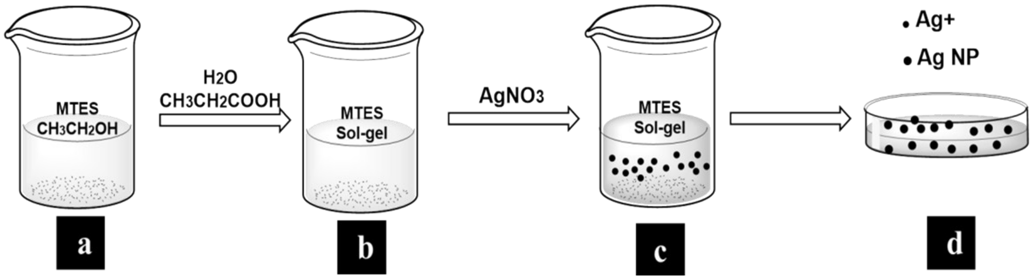

Scheme S1 Preparation scheme of Ag Ormosil glasses.

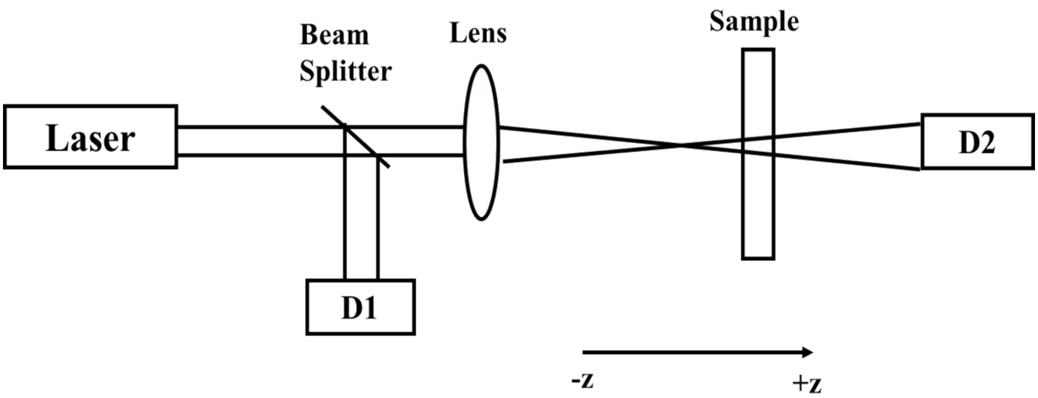

Figure S1 The optical system of Z-scan measurements.

Z-scan measurements of Ag NPs Ormosil glasses are carried on the above optical systems[1, 2]. When Gaussian laser works, it is separated into two beams. One beam is collected and recorded by detector D1 as reference laser; the other is focused by a lens, across the sample and recorded by detector D2 as detected laser. The sample is fixed on anchor, moved with the controller. The sample positions are recorded and the transmittance (ratios of D2 and D1) change with positions. Finally, the transmittance versus positions curve would be got. All samples are measured at room temperature. The Z-scan curve can be transformed into OL curve by the following model:

$$E(z) = \frac{I_0}{S_{(z)}} \quad (1)$$

$$S_{(z)} = \pi\omega_{(z)}^2 \quad (2)$$

$$\omega_{(z)} = [\left(f + \frac{z^2}{f}\right)\frac{\lambda}{\pi}]^{1/2} \quad (3)$$

Where *f* is focal parameter, obtained by fitting the Z-scan curve. Put formulas (2) and (3) into (1), then a series of E (z) values to sample positons z can be obtained. Finally, the OL curve [normalized transmittance/ E (z)] can be plotted because the normalized transmittance is certain corresponding to the certain position.

Z-scan technique put forward by Sheir et al[1] could be applied on the mechanism analysis of OL based on Z-scan theory. When laser irriadates the sample, it could be assumed that a TEM^{00} Gaussian beam of beam waist radius ω_0 traveling in the +z direction, writing as:

E as $$E(z,r,t) = E_0 \frac{\omega_0}{\omega(z)} \exp\left(- \frac{r^2}{\omega^2(z)} - \frac{ikr^2}{2R_{(z)}} \right) e^{-i\phi(z,t)} \qquad (1)$$

Where the ω is the radius of the laser spot,

$$\omega^2(z) = \omega_0^2 (1 + \frac{z^2}{z_0^2}) \qquad (2)$$

$z_0 = k\omega_0^2/2$ is the diffraction length of the beam, k=2π/λ and λ is the wavelength.

When aera of the apperatuer (s) is 1, the net transmission is deposited as:

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

Where β is nonlinear absorption coefficient, I_0 is the energy density at the focus (z=0), and L_{eff} is the effective thickness of the sample.

$$L_{eff} = [1 - \exp(-\alpha L)]/\alpha \qquad (4)$$

Where α is the linear absorption coefficient and L is the thickness of sample. The opened apperature data could be fitted with equation (3) and determine β values.

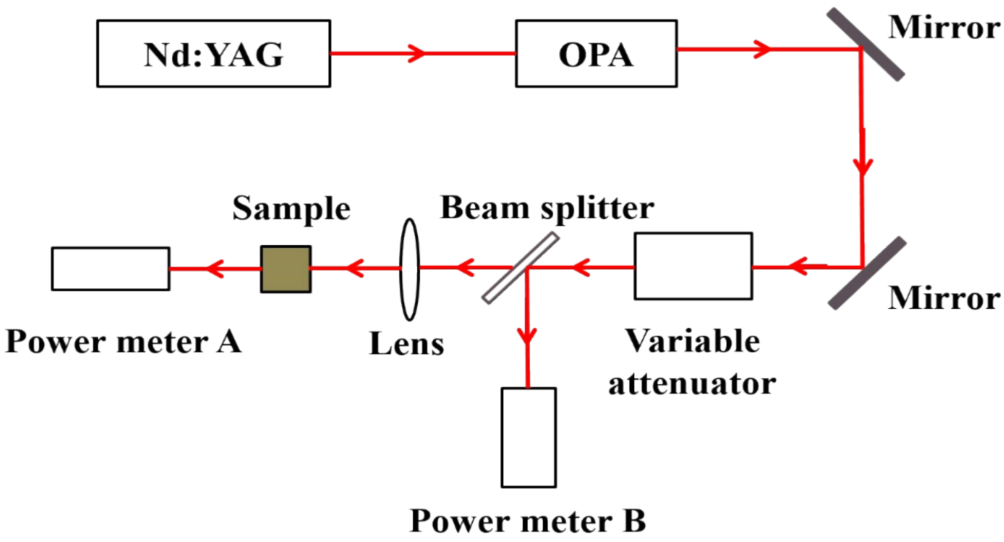

Figure S2 The optical system of optical limiting measurements by nonlinear transmittance.

The OL properties of Ormosil glasses are investigated in the following optical system[3]. The laser source is an 8 ns Nd: YAG laser and its reciting frequency is 10 Hz. When the laser works, it is reflected by mirrors to the variable attenuator and separated into two beams. One beam is focused by a lens, across the sample and recorded by power detector A as output axis; the other beam is recorded by power detector B as the input axis. Rotate the varied attenuator, and energy density would change and then a series data of input and output axis would be got. When the measurement starts, the sample is fixed onto anchor and measured at room temperature.

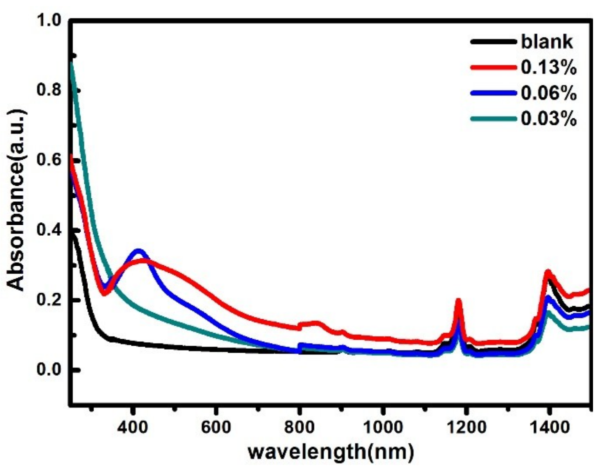

Figure S3 UV-vis-NIR absorbance spectra of Ag NPs Ormosil glasses with different doping amounts.

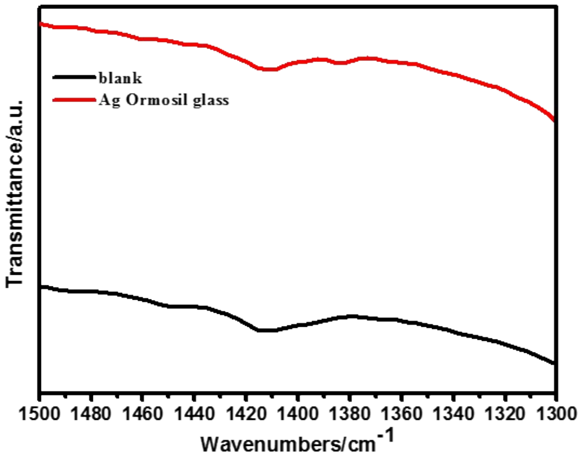

Figure S4 The FTIR of blank and Ag NPs Ormosil glasses in 1500- 1300 cm^{-1}.

The FITR spectra of blank and Ag NPs Ormosil glasses are studied in 1500-1300 cm^{-1}, and there is no $[NO_3]^-$ peak in Ag-MTES spectrum. Therefore, the $[NO_3]^-$ (1380 cm^{-1}) [4] disappeared during the aging of Ormosil glasses.

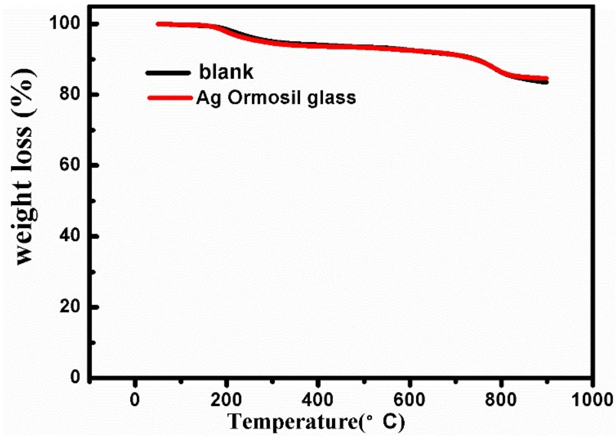

Figure S5 The thermal gravimetric curve of Ag NPs Ormosil glass.

The sample has a gradual weight loss from 50°C to 500°C at 4.9 wt% for the decomposition of methyl group on silicon atoms [5, 6]. Then, the weight loss increased to 12 wt% weight at 800°C because of water and ethanol resulting from the condensation.

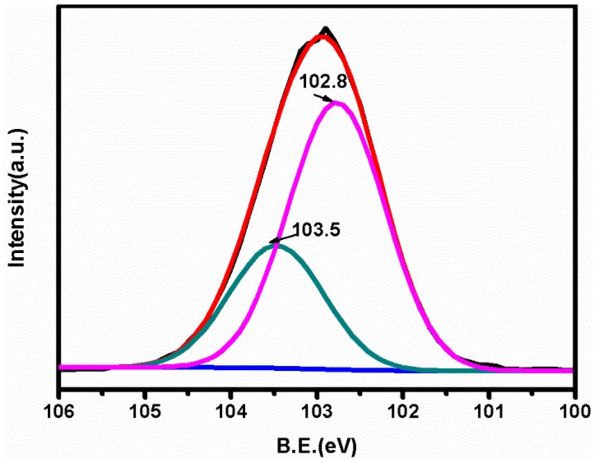

Figure S6 XPS of Si (2p) for MTES Ormosil glass.

The XPS of Si (2p) for Ormosil glass without Ag NPs is shown in Figure S6. The spectra include two peaks at 103.5 and 102.8 eV, corresponding to Si-O and Si-C, and ratio of two peaks is 1/1.5 confirming the chemical structure of MTES molecule network.

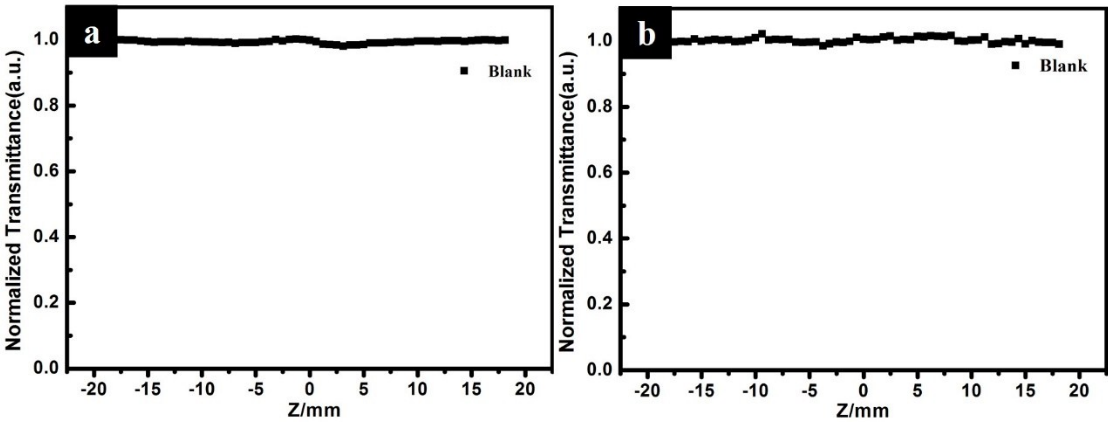

Figure S7 Z-scan measurement of blank glass under different lasers: 532 nm (a) and 1064 nm (b).

The blank Ormosil glasses without any Ag NPs are set as the standard samples to compare the Z-scan curves and measured with the same method of Ag NPs Ormosil glasses under 532 nm and 1064 nm lasers. The curves show no fluctrations with movements of sample, implying the NLA comes from the Ag NPs in Ormosil glasses.

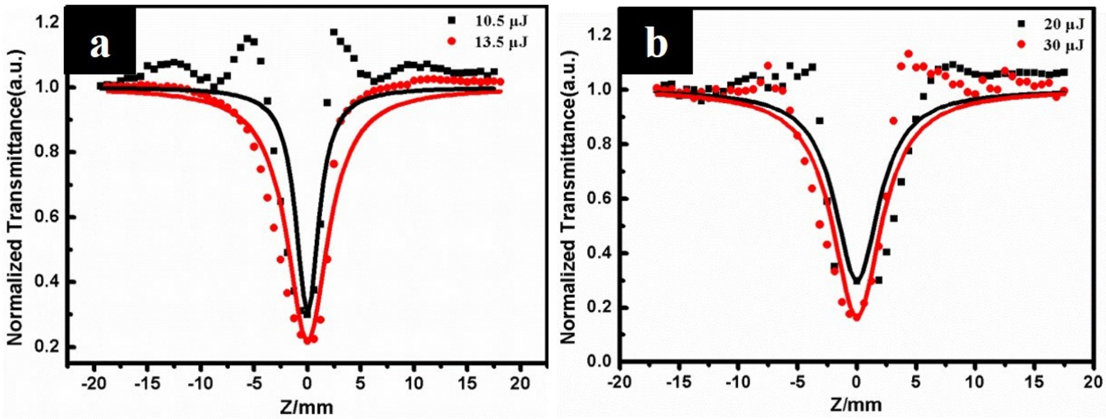

Figure S8 Z-scan patterns of Ag NPs Ormosil glasses under different laser powers at 532 nm (a) and 1064 nm (b).

Table S1 β of Ag NPs Ormosil glasses under different laser powers under 532 nm and 1064 nm.

wavelength/nm	**laser power/μJ**	**β value/cm·GW^{-1}**
532	10.5	134
	13.5	275
1064	20.0	480
	30.0	629

Table S2 β of materials based on silver materials.

Materials	**Wavelength/nm**	**β/cm·GW^{-1}**	**Reference**
{[Ag(btx)]NO_3}n_2	532	161	[7]
Ag-NPs-AZO	532	4.8	[11]
[Et4N]$_3$[MOS_3(m3-I)$(AgI)_3$] (Mo, 1; W, 2)	532	100 (1) 120 (2)	[8]
Au/Ormosil glass	532 1064	54.34 37.01	[12]
Ag/PVA/TEOS	532	12.58	[10]
Ag NP Ormosil glasses	**532** **1064**	**275** **629**	**this work**

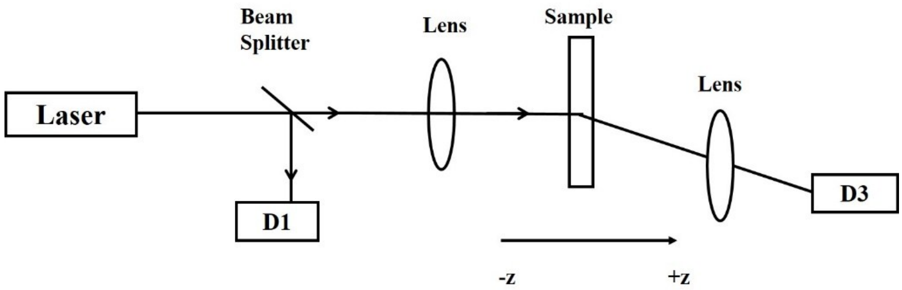

Figure S9 The nonlinear scattering measurement setup.

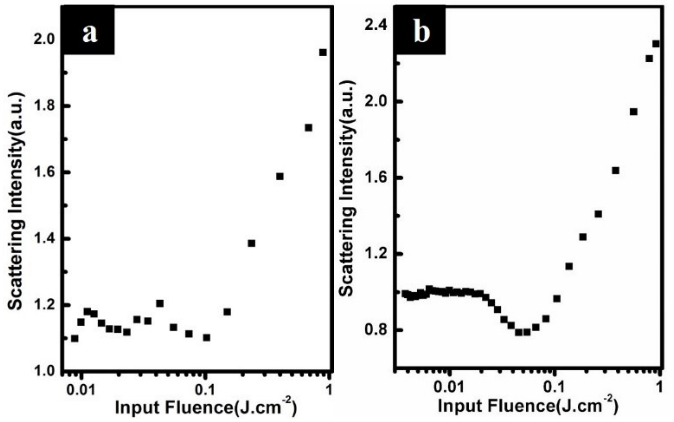

Figure S10 Scattering patterns of Ag Ormosil glasses under different laser powers under 532 nm (a) and 1064 nm (b).

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