

# Nonlinear optical limiting effect of graphene dispersions at 3.8 $\mu\text{m}$

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We investigate the nonlinear optical limiting effect of novel graphene dispersions and graphene dispersions in carbon tetrachloride at a wavelength of 3.8  $\mu\text{m}$ . The transmittances of graphene dispersions in carbon tetrachloride under two different concentrations (0.004 and 0.008 mg/mL) and two different solution thicknesses (10 and 20 mm) are measured. The influences of concentration and thickness on the optical limiting effect of graphene dispersion are analyzed. Theoretical analysis of the experimental data shows that the main optical limiting mechanism of the new graphene dispersions is Mie scattering. The limiting capacity coefficient of the new graphene dispersion in carbon tetrachloride reaches 0.405 and the minimum transmittance reaches 0.292 when the concentration is 0.004 mg/mL and the thickness is 20 mm. The graphene dispersions in carbon tetrachloride can be used to achieve good nonlinear optical limiting effects at the wavelength of 3.8  $\mu\text{m}$ .

**Keywords:** nonlinear optical limiting; nonlinear scattering; graphene dispersion.

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## 1. Introduction

With the wide application of high-power, high-intensity, and short-pulse lasers in industrial and military fields, the related optical limiting and protection materials have also begun to flourish. In particular, optical limiting materials, including phase change materials, and linear and nonlinear optical limiting (NOL) materials<sup>[1]</sup>, have been the focus of research for many years<sup>[2]</sup>. Among them, NOL materials have received extensive attention due to their excellent optical effects. Compared with other materials, NOL materials usually have the advantages of a high damage threshold and a short response time. More importantly, some NOL materials have a wide operating wavelength range, which makes them suitable for wide-band optical limiting. Among the common NOL materials, semiconductors<sup>[3]</sup> and organic materials<sup>[4,5]</sup> have been widely studied for several decades. Some new NOL materials such as inorganic metal clusters<sup>[6,7]</sup>, carbon nanotubes<sup>[8,9]</sup>, and composite nanomaterials<sup>[10,11]</sup> have developed rapidly in recent years<sup>[12-14]</sup>. However, the previous reports on NOL materials have mainly focused on the visible and near-infrared region, while there are few reports about NOL within the mid-infrared

region (especially at the wavelength of 3–5  $\mu\text{m}$ ). The NOL within the mid-infrared region is important, as it can be used to protect the human eye and some sensitive sensors from high-power mid-infrared lasers in many fields such as the military field, biomedicine, and material processing. We have recently achieved good optical limiting effect of 3–5  $\mu\text{m}$  by using an  $\text{As}_2\text{Se}_3$  fiber<sup>[15]</sup>, but in general the fibers are difficult to apply to the large-area laser limiting due to their small core size.

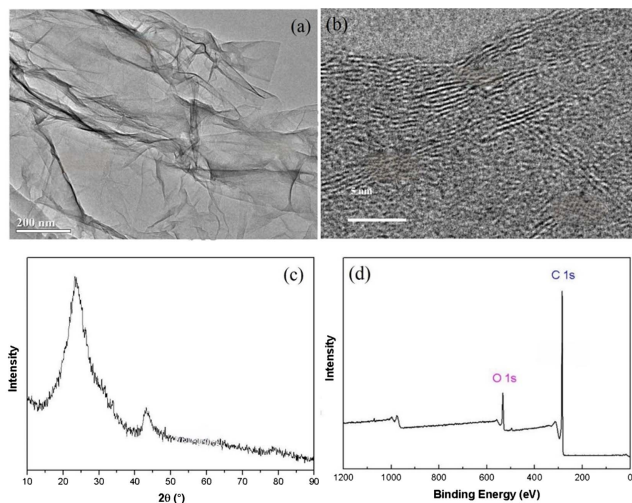
In this study, we present a novel mid-infrared laser optical limiting suspension, graphene dispersion in carbon tetrachloride, at the wavelength of 3.8  $\mu\text{m}$ . Unlike other optical limiting materials such as optical fibers and phase change films, graphene dispersion in carbon tetrachloride is not limited by material size and the preparation process and can be used for large-area mid-infrared laser limiting. The optical limiting effect of graphene dispersions in carbon tetrachloride is measured at the wavelength of 3.8  $\mu\text{m}$ . In our experiments, graphene dispersions in carbon tetrachloride under two different concentrations (0.004 and 0.008 mg/mL) and two different thicknesses (10 and 20 mm) are used. These experimental results demonstrate that graphene dispersions in carbon tetrachloride may be a promising NOL material at 3.8  $\mu\text{m}$ .

## 2. Experimental Setup

In the experiment, the graphene material is high-temperature-reduced graphene oxide; the characterization images of the graphene are shown in Fig. 1. The microscopic morphology of graphene nanosheets can be obtained by analyzing transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images, and the purity of graphene nanosheets can be obtained by analyzing X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) patterns. The thickness of graphene nanosheets is about 0.8 nm, the diameter is 0.5–5  $\mu\text{m}$ , purity is about 99%, and the single-layer ratio is more than 80%. Graphene material and the above information are obtained from Nanjing XFNano Materials Tech Co., Ltd. (Nanjing, China). When preparing the dispersion, we first weighed 0.1 mg of graphene, then dissolved it in 10 mL of carbon tetrachloride liquid to make a dispersion with a concentration of 0.01 mg/mL. To ensure the uniformity of the dispersion, the resultant dispersions were sonicated at 40 kHz for 30 min. Then a certain amount of carbon tetrachloride was added to the dispersion of 0.01 mg/mL according to the experimental requirements to prepare a dispersion with the specific concentration. The diluted dispersion was sonicated at 40 kHz for 30 min again. The final experimental dispersion is very homogeneous and does not precipitate within 8 h.

According to the transmittance at the 3.8  $\mu\text{m}$  wavelength, and considering the safety of the experiment, carbon tetrachloride was selected as the solvent, which has the advantages of high solubility and low toxicity. We prepared two kinds of graphene dispersions in carbon tetrachloride with different concentrations of 0.004 mg/mL and 0.008 mg/mL. The parameters of the prepared graphene dispersions are shown in Table 1.

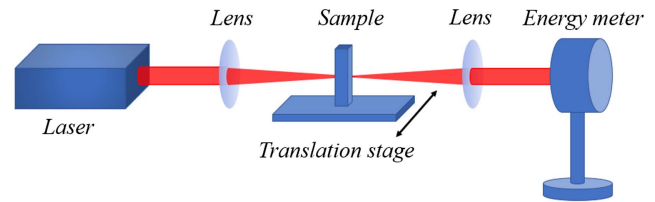
The experimental setup used to evaluate the NOL performance of graphene dispersion is shown in Fig. 2. A solid-state pulsed laser with a wavelength of 3.8  $\mu\text{m}$  was used as the light



**Fig. 1.** Characterization images of experimental graphene. (a) TEM image of single-layer graphene; (b) HRTEM image of single-layer graphene; (c) XRD pattern of single-layer graphene; (d) XPS pattern of single-layer graphene.

**Table 1.** Parameters of Two Graphene Dispersions.

Number	Concentration (mg/mL)	Solute	Solvent (50 mL)
1	0.004	Graphene (0.2 mg)	Carbon tetrachloride
2	0.008	Graphene (0.4 mg)	Carbon tetrachloride



**Fig. 2.** Schematic diagram of the experimental setup.

source in the transmittance measurement. The repetition frequency and pulse width of the laser were set as 1 Hz and 12 ns, respectively. The probe beam passed through a lens and then through the sample positioned in the focal plane of the lens. The laser beam passing through the sample cell was converged with another lens and recorded with an energy meter. The focal length of the lens was 80 mm, and the area of the laser spot on the sample was 0.0025  $\text{cm}^2$ . The sample was placed on a translation table, which makes it possible to move perpendicularly to the light propagation direction. The incident and transmission energies of the sample were measured by the energy meter when the sample was removed from the optical path and irradiated by the laser, respectively. Therefore, the transmittance of the graphene dispersion sample can be obtained by comparing the ratio of the energy on the energy meter with and without the sample in the optical path. The time interval between these two measurements was about 20 s. Since the root mean square error (RMSE) output energy of the laser within 30 s is less than  $\pm 1.5\%$ , the transmittance measurement uncertainty due to laser energy instability was  $\pm 1.5\%$ . In each measurement, 20 data points were recorded and averaged to reduce measurement uncertainty. The transmittances of the graphene dispersion corresponding to different input fluence can be obtained by gradually increasing the laser output energy.

## 3. Experimental Results and Discussion

To accurately evaluate the NOL ability of graphene dispersions, we define the optical limiting capacity coefficient  $\delta$  as<sup>[16]</sup>

$$\delta = T_{\max} - T_{\min}, \quad (1)$$

where  $T_{\max}$  is the linear transmittance of nonlinear material, and  $T_{\min}$  is the minimum stable laser transmittance of nonlinear

material with optical limiting effect. From Eq. (1), we can know that the larger the  $\delta$ , the stronger the optical limiting effect of the graphene dispersions.

The transmittances of graphene dispersions at two concentrations (0.004 and 0.008 mg/mL) are depicted in Fig. 3. When the incident laser energy density is low (less than 0.1 J/cm<sup>2</sup>), the transmittances of the graphene dispersions are relatively high, which are almost larger than 0.6. When the input fluence increases gradually, the graphene dispersions gradually exhibit NOL characteristics, and the transmittance decreases with the increase of the incident energy density. In Fig. 3(a), when the thickness of graphene dispersion is 10 mm, for the graphene dispersions with the concentration of 0.004 and 0.008 mg/mL, the limiting thresholds are, respectively, 0.13 and 0.14 J/cm<sup>2</sup>, the minimum transmittances are, respectively, 0.365 and 0.292 when the input fluence is 1.37 J/cm<sup>2</sup>, and the  $\delta$  are, respectively, 0.387 and 0.405. The results show that the graphene dispersion with higher concentration can achieve better NOL performance, though it has a lower linear transmittance. The situation in Fig. 3(b) is similar to that in Fig. 3(a). When the thickness of graphene dispersion is 20 mm, for the graphene dispersions with the concentration of 0.004 and 0.008 mg/mL, the limiting thresholds are, respectively, 0.14 and 0.15 J/cm<sup>2</sup>, the minimum transmittances are, respectively, 0.296 and 0.264 when the maximum input fluence is 1.37 J/cm<sup>2</sup>, and the  $\delta$  are, respectively, 0.391 and 0.356. The optical limiting performance of graphene dispersions is positively correlated with concentration.

We also compare the influence of thickness on the optical limiting ability of graphene dispersions. In Fig. 4, we show the transmittance of graphene dispersions at the same concentration for two different thicknesses. As shown in Figs. 4(a) and 4(b), both the minimum transmittance  $T_{\min}$  and the linear transmittance  $T_0$  decrease with the increase of sample thickness. It can be simply understood that as the sample thickness increases, the laser has more chance to touch graphene on the way forward. In Fig. 4(a), the slope of the transmittance curve with the thickness of 20 mm is smaller than that of the thickness of 10 mm when the input fluence is in the range from 0.13 J/cm<sup>2</sup> to 0.78 J/cm<sup>2</sup>, while the slope of the transmittance curve with the thickness of 20 mm is larger than that of the thickness of 10 mm when the input fluence is in the range from 0.78 J/cm<sup>2</sup> to

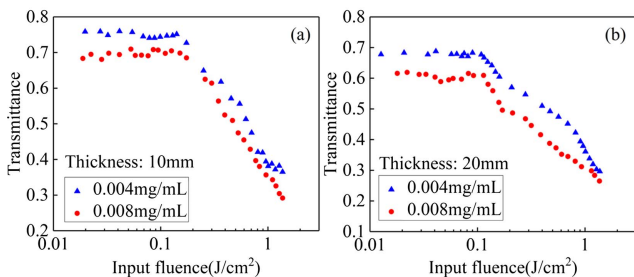


Fig. 3. Transmittances of graphene dispersions at two different concentrations with thickness of (a) 10 mm and (b) 20 mm.

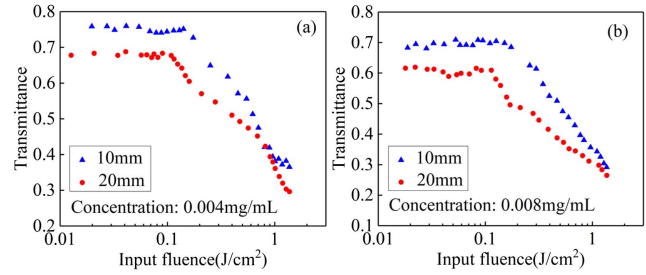


Fig. 4. Transmittances of graphene dispersions at two different thicknesses with concentration of (a) 0.004 mg/mL and (b) 0.008 mg/mL.

1.58 J/cm<sup>2</sup>. In Fig. 4(b), the slope of the transmittance curve with the thickness of 20 mm is smaller than that of the thickness of 10 mm when the input fluence is in the range from 0.15 J/cm<sup>2</sup> to 1.58 J/cm<sup>2</sup>. In this case, we speculate that the optical limiting mechanism of graphene-carbon tetrachloride dispersion may be Mie scattering. For Mie scattering, under the same other conditions, the more bubbles produced by laser or the larger the bubble radius, the faster the transmittance curve decreases with the increase of incident fluence<sup>[17]</sup>. When the other conditions are same, the thicker the dispersion, the more scattering sources in the dispersion, which will enhance the optical limiting capacity of the dispersion. However, the thicker dispersion will reduce the average energy density obtained by each scattering source and thus results in smaller radius of bubbles in the dispersion, which will weaken the optical limiting capacity of the dispersion. Therefore, there is no simple linear relationship between thickness and optical limiting capacity.

In Table 2, we present the experimental results of graphene dispersion with two different concentrations (0.004 and 0.008 mg/mL) and two different thicknesses (10 and 20 mm). According to the experimental results, it can be seen that the graphene-carbon tetrachloride dispersion has an obvious optical limiting effect at 3.8  $\mu\text{m}$ . In the next section, we will try to find out the reason for the optical limiting effect.

#### 4. Theoretical Discussion

According to the existing experimental results at other wavelengths, we know that the NOL mechanisms of graphene dispersions are complex, including nonlinear scattering, antisaturable absorption, and multiphoton absorption<sup>[18]</sup>. When the concentration of graphene dispersion is not very high, the main nonlinear effect is Mie scattering<sup>[19]</sup>. According to the theory of standard Mie scattering, each scattering source in the graphene dispersion can be equivalent to the standard sphere model. The extinction cross section  $Q_{\text{ext}}$ , scattering cross section  $Q_{\text{sca}}$ , and absorbing cross section  $Q_{\text{abs}}$  of a single scattering source can be, respectively, expressed as<sup>[20]</sup>

$$Q_{\text{ext}} = \left( \frac{\lambda^2}{2\pi^2 r^2} \right) \sum_{k=1}^{\infty} (2k + 1) \text{Re}[a_k + b_k], \quad (2)$$

**Table 2.** Experimental Results of Graphene Dispersion.

Number	Concentration (mg/mL)	Thickness (mm)	Linear Transmittance	Minimum Transmittance	$\delta$	Limiting Threshold ( $J/cm^2$ )
1	0.004	10	75.2%	36.5%	0.387	0.13
2	0.004	20	68.7%	29.6%	0.391	0.14
3	0.008	10	69.7%	29.2%	0.405	0.14
4	0.008	20	62.1%	26.4%	0.356	0.15

$$Q_{sca} = \left( \frac{\lambda^2}{2\pi^2 r^2} \right) \sum_{k=1}^{\infty} (2k+1)(|a_k|^2 + |b_k|^2), \quad (3)$$

$$Q_{abs} = Q_{ext} - Q_{sca}, \quad (4)$$

where  $r$  is the radius of the scattering source, and  $\lambda$  is the wavelength of the incident wave. The  $k$  is an integer, and  $\text{Re}[a_k + b_k]$  means the real part of  $a_k + b_k$ . The  $a_k$  and  $b_k$  are the Mie scattering coefficients<sup>[21]</sup>, which can be, respectively, expressed as

$$a_k = \frac{m^2 j_k(mx) [x j_k(x)]' - j_k(x) [mx j_k(mx)]'}{m^2 j_k(mx) [x h_k^{(1)}(x)]' - h_k^{(1)}(x) [mx j_k(mx)]'}, \quad (5)$$

and

$$b_k = \frac{j_k(mx) [x j_k(x)]' - j_k(x) [mx j_k(mx)]'}{j_k(mx) [x h_k^{(1)}(x)]' - h_k^{(1)}(x) [mx j_k(mx)]'}, \quad (6)$$

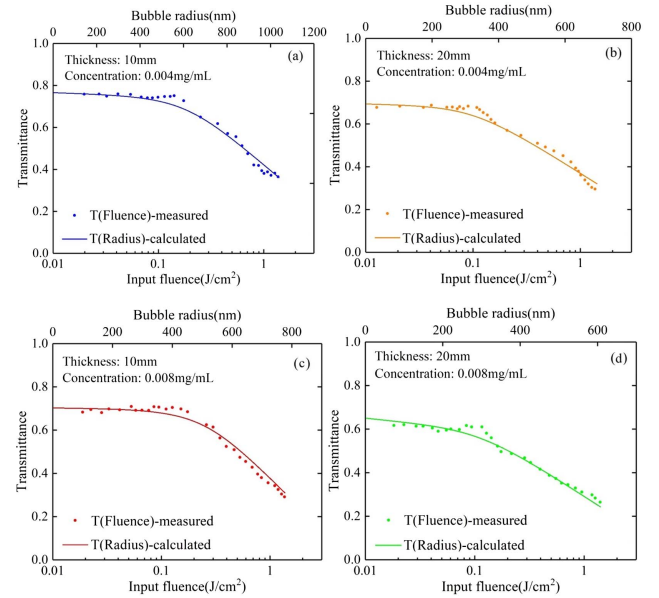
where  $m$  is the complex refractive index of scattering sources. The functions  $j_k(z)$  and  $h_k^{(1)} = j_k(z) + iy_k(z)$  are spherical Bessel functions of order  $k$  ( $k = 1, 2, \dots$ ) and of the given arguments,  $z = x$  or  $mx$ , respectively, and the primes mean derivatives with respect to the argument.

When Mie scattering effects occur in the graphene dispersion, according to the Beer–Lambert law, the transmittance  $T_L$  is given by [22,23]

$$T_L = T_0 e^{-0.2M_g Q_{ext} L / (M_s V)}, \quad (7)$$

where  $T_0$  is the linear transmittance,  $M_g$  is the total mass of graphene in the dispersion,  $M_s$  is the mass of a single graphene nanosheet,  $V$  is the volume of dispersion, and  $L$  is the thickness of the graphene dispersion. According to Eqs. (2) and (7), when Mie scattering occurs, the transmittance of the material is directly related to the radius of the scattering source (usually bubbles in the dispersion).

According to Eqs. (2)–(7), we can obtain the relationship between the transmittance  $T_L$  and the bubble radius  $r$ . The transmittances of graphene dispersions changing with the bubble radius and input fluence are shown in Fig. 5. In Fig. 5, the relationship between the calculated transmittance and the bubble radius corresponding to each experimental case is



**Fig. 5.** Transmittance changes with incident fluence (solid dots) and bubble radius (solid line) under different sample thicknesses and concentrations. (a) 10 mm, 0.004 mg/mL; (b) 20 mm, 0.004 mg/mL; (c) 10 mm, 0.008 mg/mL; (d) 20 mm, 0.008 mg/mL.

represented by a solid curve. At a relatively low incident laser energy density, the radius of the bubble gradually increases with the increase of the input fluence. In addition, when comparing the four graphs in Fig. 5, it can be found that when Mie scattering occurs, under the same transmittance, the higher the dispersion concentration, the smaller the bubble radius<sup>[24]</sup>. For this phenomenon, the possible reason is that with the increase of concentration, the number of bubbles generated in the dispersion also increases sharply, and many bubbles have been replaced by new bubbles before they expand, so the average radius of the bubbles decreases significantly<sup>[25,26]</sup>. Comparing the theoretical curve and the experimental results in the four figures, we find the Mie scattering theory is in good agreement with our experimental results, which indicates that the main optical limiting mechanism of graphene dispersions in carbon tetrachloride at 3.8  $\mu\text{m}$  wavelength is Mie scattering.

According to Eqs. (2)–(4), we can calculate the nonlinear scattering coefficient and nonlinear absorption coefficient under

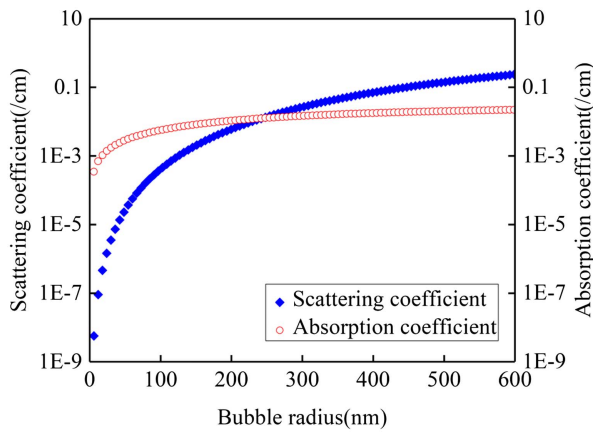


Fig. 6. Scattering and absorption coefficients versus bubble radius.

different bubble radii. The calculated results for the graphene dispersions at the concentration of 0.004 mg/mL and the thickness of 10 mm are shown in Fig. 6. As shown in Fig. 6, when the bubble radius is small (less than 100 nm), the absorption coefficient is several orders of magnitude larger than the scattering coefficient. With the increase of incident energy density, the growth rate of the scattering coefficient is much faster than that of the absorption coefficient, and the scattering coefficient is finally greater than that of the absorption coefficient. When the bubble radius is larger than 250 nm, the scattering coefficient is larger than the absorption coefficient, and the transmittance change of the suspension is mainly due to scattering. This calculation result further indicates that the main optical limiting mechanism of graphene dispersions in carbon tetrachloride at 3.8 μm wavelength is Mie scattering. The theoretical calculation results shown in the Figs. 5 and 6 are also consistent with our analysis results in Section 3.

According to the experimental results, we can find when the concentration of graphene dispersions in carbon tetrachloride is 0.004 mg/mL and the thickness is 20 mm, the optical limiting capacity coefficient  $\delta$  is 0.405, and the minimum transmittance  $T_{\min}$  is 0.292. In Table 3, we compare graphene dispersions in carbon tetrachloride with some other optical limiting materials. Although the values of  $\delta$  and  $T_{\min}$  of graphene dispersion at the mid-infrared region are worse than those of some fiber<sup>[15]</sup>, it is

still better than those of some other optical limiting materials such as graphene oxide dispersion<sup>[27]</sup>, special optical glass<sup>[28]</sup>, and nonlinear optical crystals<sup>[29]</sup>. These results show that graphene dispersions in carbon tetrachloride have an excellent optical limiting effect in the mid-infrared region.

### 5. Conclusion

In summary, we present a new graphene dispersion in carbon tetrachloride, and experimentally research the NOL effect of the dispersion at the wavelength of 3.8 μm. The transmittances of graphene dispersion under two concentrations (0.004 and 0.008 mg/mL) and two solution thicknesses (10 and 20 mm) are measured experimentally. The influence of concentration and thickness on the optical limiting ability of graphene dispersion is analyzed. The experimental results show that graphene dispersion has good limiting performance for a pulsed laser with a typical infrared wavelength of 3.8 μm. Further, the experimental data indicate that the optical limiting effect of the graphene dispersion is mainly due to Mie scattering. The limiting capacity coefficient of the graphene dispersions in carbon tetrachloride reaches 0.405, and the minimum transmittance reaches 0.292. The results show graphene dispersion may be a promising material for NOL at the wavelength of 3.8 μm.

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Table 3. Comparison of Optical Limiting Properties of Several Materials.

Materials	$\delta$	$T_{\min}$	Wavelength	References
Graphene dispersions in carbon tetrachloride	0.405	0.292	3.8 μm	This article
0.5 m As <sub>2</sub> Se <sub>3</sub> fiber	0.893	0.123	3.6 μm	[15]
Graphene oxide dispersions in N-methylpyrrolidone	0.385	0.423	1.75 μm	[27]
Graphene oxide Ormosil glasses	0.316	0.184	1.57 μm	[28]
ZnGeP <sub>2</sub>	0.286	0.591	4.1 μm	[29]

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