Nonlinear Properties Of Water-soluble Ag$_2$S And PbS Quantum Dots Under Picosecond Laser Pulses

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Abstract. In this paper, the water-soluble Ag$_2$S and PbS quantum dots(QDs) are synthesized by aqueous phase synthesis. The nonlinear optical properties of Ag$_2$S and PbS QDs were investigated by Top-hat Z-scan technique under ps laser pulses (λ =532 nm, t=21 ps). The open Z-scan results show that Ag$_2$S and PbS QDs all have a valley value which indicate that they have strong reverse saturable absorption(RSA). The nonlinear absorption coefficient of Ag$_2$S QDs is $6.72 \times 10^{-13}$ esu, however, the valley value of PbS QDs at the focal point is similar to 1, so its nonlinear absorption coefficient is small, is $7.13 \times 10^{-14}$ esu. The close Z-scan results show that Ag$_2$S QDs has self-defocusing effect and PbS QDs has self-focusing effect, their nonlinear refractive index are on the order of $-6.13 \times 10^{-13}$ esu and $2.41 \times 10^{-13}$ esu. After fitting calculation, the third order nonlinear polarizability of Ag$_2$S and PbS QDs are $2.40 \times 10^{-14}$ esu and $6.02 \times 10^{-15}$ esu respectively. The physical mechanisms responsible for the nonlinear optical response of the QDs are discussed in detail. In summary, the nonlinear absorption and refraction properties of Ag$_2$S QDs are better than that of PbS QDs, but both of these materials are of great significance for the research of photoelectric, biosensor, optical limiting, and self-adaptive technologies.

1. Introduction
In recent years, with the continuous development of optoelectronics, nonlinear optics has become an indispensable part of optoelectronics and has also formed a series of interdisciplinary studies with other fields of research [1]. Due to their unique quantum confinement effect, surface effect and strong nonlinear optical effect, semiconductor QDs materials have shown a very wide range of applications in optical switching, optical limiting, optical communications and other fields [2][3][4]. Therefore, the research on the photophysical properties of semiconductor QDs has become a research front in the 21st century. For example, the optical mixing technique is used to measure the nonlinear parameters of semiconductor materials. The Ag$_2$S QDs is one of the most in-depth study materials, and is a semiconductor of I-IV family which has a density of 6.85 to 7.23 and a melting point of 825 °C. The linear refractive index of Ag$_2$S QDs is 2.2, and the linear transmittance is 75% under the experimental conditions [5][6]. In 2016, Aleali et al. used nanosecond Z-scan technology to study the nonlinear optical properties of Ag$_2$S colloids at a wavelength of 532 nm, demonstrating that the threshold limit of Ag$_2$S colloid decreases as the Ag$_2$S nanoparticle concentration increases [7]. In recent years, as nanotechnology research continues to be valued by all the countries in the world, Ag$_2$S QDs has an important application in sensors, biomedicine and liquid lubrication [8]. PbS QDs is a direct wide-bandgap semiconductor of IV-VI family with a forbidden band width of 0.41 eV at room temperature. Its quantum size effect can be observed at 18 nm. Its crystal structure is blue cubic crystal with a density of 7.5 and a melting point of 1114 °C soluble acid and organic solvents. The linear refractive index of PbS QDs is 3.9, its electron and hole radius are about 10 nm, so its optical nonlinearity is greatly
enhanced in the strong region [9]. Based on this feature, it has a wide range of applications in optical information storage and fast communication switching devices.

Researching the nonlinear optical characteristics of Ag$_2$S and PbS QDs are attracting people’s attention. In order to study the nonlinear properties of Ag$_2$S and PbS QDs under ps laser pulse, we research the nonlinear absorption characteristics and the nonlinear refraction characteristics of Ag$_2$S and PbS QDs using top-hat z-scan technology under 21 ps laser pulse width at 532 nm.

2. Samples
Preparation and Characterization of Ag$_2$S QDs: Preparation process of water-soluble Ag$_2$S QDs is shown in Figure 1. 400 ml of deionized water was bubbled through nitrogen for 20 min to remove oxygen from the water. 1.089 ml of 3-mercaptopropionic acid (3-MPA) was added to deoxygenated deionized water. The pH of the solution was adjusted to 7.5 using 2 mol/L NaOH and 2 mol/L acetic acid and the temperature was set to 90 °C. Then 0.2125 g of AgNO$_3$ was added to the solution, and the pH was adjusted to 7.5. The temperature was raised to 90 °C, weighed 0.075 g Na$_2$S $\cdot$ H$_2$O dissolved into 100 ml pre-prepared deoxygenated water, with a constant pressure funnel slowly added (about 40 min), reflected after 3 hours to stop. After centrifugation, the resulting solution was spiked with appropriate deionized water, stored in the dark and kept at 4 °C for later analysis.

![Figure 1. Process of preparation of Ag$_2$S QDS](image)

The characterization was carried out by centrifugation of the resulting Ag$_2$S-3 MPA QDs under natural conditions of darkness at room temperature for the analysis of infrared light and fluorescence spectra as shown in Figure 2 (a) (b).

![Figure 2. The infrared spectra (a) and fluorescence spectra (b) of Ag$_2$S QDs](image)

The Ag$_2$S-3 MPA quantum dots are prepared by slowly adding a sulfur source to a mixture of 3-mercaptopropionic acid and silver sulfide in an aqueous solution. The color of the solution turned yellow with the addition of the sulfur source and gradually turned dark brown with the addition of the sulfur source. The crystal structure of the formed nanoparticles is characterized by powder X-ray diffraction as shown in Figure 3.
Preparation and Characterization of PbS QDs: Take 200 ml deionized water into the three-necked flask at room temperature and accurately add 138 μl of thioglycolic acid to it. The above solution was purged with nitrogen for 30 min and adjusted to pH 9.0 with 1 mol/L NaOH solution. Weigh 1.656 g Pb(NO₃)₂ powder and dissolve it in 50 ml deionized water to make 0.1 mol/L Pb(NO₃)₂ Solution, take good Pb(NO₃)₂ solution 40 ml added to the pH-adjusted thioglycolic solution was stirred in a large amount of yellow-green precipitate formed, continue to adjust the solution pH to 9.0; with the addition of NaOH, The precipitate gradually disappear, the solution becomes clear and transparent. Adjust the temperature of the solution system, the temperature was raised to 100 °C, with vigorous stirring with a constant pressure funnel slowly dropping 15 mmol/L Na₂S solution 80 ml, the solution gradually changed from the clarified to tan, to prove the formation of PbS QDs.

The prepared PbS QDs was centrifuged and washed for fluorescence spectroscopy, and the fluorescence wavelength was measured at an excitation wavelength of 600 nm. The obtained fluorescence spectrum is shown in Figure 4.
3. Experimental device

Figure 5 shows experimental device. In our experiment, ps Nd: YAG laser (EKSPLA) is used as the light-source that provides 21 ps laser pulse width at 532 nm with a repetition rate of 10 Hz. The laser output laser beam waist radius is 21μm and the aperture linear transmittance is 0.21.

![Experimental Device Diagram]

A1, A2: aperture; D1, D2, D3: detectors

Figure 5. The system model of Top-hat Z-scan

In the experiment, the attenuated laser pulse through the lens to focus on the sample, and change the position of the sample on the optical axis. The light passing through the sample is split into two beams by a beam splitter, and the reflected light enters detector D1 to measure the nonlinear absorption characteristic of the sample, that is an open aperture Z-scan; the light transmitted through the beam splitter passes through an adjustable size of the hole, is received by the detector D2 to detect the nonlinear refraction characteristics, namely closed aperture Z-scan. The open aperture and closed aperture Z-scan characteristic curves are shown in Figure 6 and Figure 7.

4. Theoretical Analysis

After the Top-hat beam converges, its horizontal distribution of light field can be written as [10]:

\[ E(r, z, t) \propto \exp \left[ -\frac{r^2}{2\sigma^2} \right] \exp \left[ \frac{imr^2}{\lambda z} \right] \]

(1)

Among them, \( r \) is horizontal polar, \( J_1(\cdot) \) is coordinates for the first-order Bessel function. Therefore, the beam waist radius takes the same expression equation as [11][12], \( \omega_0 = \frac{\lambda f}{d} \), the diffraction length of the beam is \( z_0 = \frac{\pi \omega_0^2}{\lambda} \).

Top-hat baffle Z-scan is similar to the traditional Z-scan theory, in order to discuss the simplification of the problem, here we only consider the third-order nonlinear refraction. The relationship between the light intensity and the phase of the sample is as follows:

\[ \Delta \phi = k l \gamma \]

(2)

Where, \( \Delta \phi \) is the phase change, \( z' \) is the light beam propagation depth in the sample, \( I \) is the light intensity in the sample, and \( \gamma \) is the nonlinear refractive index of the sample.

The light field distribution in the sample is:

\[ E(r, z, t) = E_0(r, z, t) \exp(-\alpha L) \exp[i\Delta \phi(r, t)] \]

(3)

The distribution of the light field at the baffle is defined as \( E_b(r_2, z, t) \), the distribution of the light field at the baffle under linear conditions is defined as \( E'_b(r_2, z, t) \). The optical field distribution at the diaphragm \( A_2 \) and baffle can be obtained by integrating Fresnel diffraction twice. Therefore, the intensity distribution \( |E_d|^2 \) of the baffle on the space and the pulse time can be integrated into the beam in D energy. Through normalization, we can get the nonlinear transmittance:

\[ T(z) = \frac{\int_{-\infty}^{x} \int_{-\infty}^{x} 2\pi r_2 |E_d|^2 dr_2 dt}{\int_{-\infty}^{x} \int_{-\infty}^{x} 2\pi r_2 |E'_d|^2 dr_2 dt} \]

(4)

In this way, fitting the curve of the nonlinear transmittance \( T(z) \) allows us to determine the nonlinear refractive index \( \gamma \) of the sample.
5. Results and discussion
As shown in Figure 2, the resulting emission wavelength of the Ag$_2$S-3 MPA QDs is in the near-infrared range and its infrared structure proves that 3-mercaptopropionic acid is linked to Ag$_2$S via a thiol group because there is no SH at 2560 cm$^{-1}$ Bonds, and peaks at 1560 cm$^{-1}$ and 1414 cm$^{-1}$ prove to demonstrate the opposite and symmetrical stretching vibration of the carboxyl group C=O of 3-mercaptopropionic acid. The 2964 cm$^{-1}$ and 2919 cm$^{-1}$ proved to be C-H symmetrical and inversely symmetric stretching vibration in the 3-mercaptopropionic acid structure.

The crystal structure of the formed nanoparticles is characterized by powder X-ray diffraction. The resulting XRD spectrum is the same as previously reported, as shown in Figure 3.

The prepared PbS QDs is centrifuged and washed for fluorescence test, and the fluorescence wavelength is measured at an excitation wavelength of 600 nm. The obtained fluorescence spectrum is shown in Figure 4. The existence of the fluorescence absorption peak indicates that the QDs has fluorescence, and its fluorescence absorption peak is between 1100 nm and 1305 nm.

In our experiment, the nonlinear absorption and refraction characteristics of Ag$_2$S QDs is studied by using Top-hat Z-scan technology under the ps laser pulses. The experimental laser energy intensity is 2.5 μJ. Under the experimental conditions, the linear transmittance is 76%. Figure 6 (a) and (b) show the results of the nonlinear absorption and refraction of Ag$_2$S QDs respectively.

Figure 6. The open (a) and close (b) aperture z-scan normalized transmittance curves of water-soluble Ag$_2$S QDs(21 ps、532 nm)

As can be seen from Figure 6 (a), the normalized transmittance decreases with increase of the beam intensity. The results show that the nonlinear absorption of the Ag$_2$S QDs is reverse saturable absorption mainly due to two-photon absorption. From Figure 6 (b) we can find that the nonlinear refractive index is positive because of bound electron. The open and closed Z-scan curves are fitted and calculated to obtain the nonlinear absorption coefficient, the nonlinear refractive index and the third-order nonlinear polarizability under the experimental conditions, as shown in Table 1.

Next, the sample is changed to the PbS QDs. The laser energy intensity is also selected 2.5, the linear transmittance of the sample under this experimental conditions is 91%, the experimental results reflecting the nonlinear absorption characteristics are shown in Figure 7 (a), the experimental results reflecting the nonlinear refractive index are shown in Figure 7 (b).
Figure 7. The open (a) and close (b) aperture z-scan normalized transmittance curves of PbS QDs (21 ps, 532 nm).

As can be seen from Figure 7 (a), the nonlinear absorption properties of PbS QDs is similar to that of Ag$_2$S QDs, shows reverse saturable absorption effect, is due to two-photon absorption. Under the experimental conditions, although PbS QDs shows reverse saturable absorption, but the focal point is similar to 1, so its nonlinear absorption coefficient is small. It can be seen from Figure 7 (b) that the nonlinear refraction of PbS is self-focusing, and the nonlinear refractive index is positive that is also mainly due to bound electron when pulse width is 21 ps. The nonlinear refractive index and the third-order nonlinear polarizability under the experimental conditions of PbS are also shown in Table 1.

Table 1. Third-order nonlinear characteristic parameters of Ag$_2$S, PbS QDs under picosecond pulse

|                        | Ag$_2$S         | PbS            |
|------------------------|-----------------|----------------|
| Nonlinear index of refraction n$_2$ (esu) | -6.13×10$^{-13}$ | 2.41×10$^{-13}$ |
| Nonlinear absorption coefficient β (m/W)   | 6.72×10$^{-13}$ | 7.13×10$^{-14}$ |
| Third order nonlinear polarizability X$^{(3)}$ | 2.40×10$^{-14}$ | 6.02×10$^{-15}$ |

6. Conclusion:
The nonlinear absorption and refraction properties of Ag$_2$S and PbS QDs have been studied using top-hat Z-scan technology under the ps laser pulses. The experimental results show that the nonlinear absorptions of the Ag$_2$S and the PbS QDs are all reverse saturable absorption and mainly due to two-photon absorption under the ps laser pulses. The nonlinear refraction characteristics of Ag$_2$S QDs are self-defocusing and the nonlinear refractive indexes are negative because of free carrier under ps laser pulses. The nonlinear refraction characteristics of PbS QDs are self-focusing and the nonlinear refractive indexes are positive because of bound electron under the ps laser pulses. Therefore, nonlinear absorption and refraction properties of Ag$_2$S QDs are better than that of PbS QDs, but both of these materials all have a wide range of applications.

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