RESEARCH ARTICLE

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Nonlinear Responses and Optical Limitation of Copper Nanoparticles by Z-scan Method

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Abstract: Recently, copper particles in nano dimensions have been gaining attention because they have advanced features and potential applications in various fields. This work studies the nonlinear optical performance of copper nanoparticles. We utilized laser ablation to create copper nanoparticles. In this technique, a piece of copper in distilled water is irradiated using the laser beam. Laser ablation was done for 30 min. The optical nonlinearities are measured by means of the Z-scan technology. The open-aperture Z-scan experiments showed that Cu nanoparticles have strong nonlinear absorption. Through a closed aperture Z-scan experiment, we could analyze the nonlinear refraction of sample. We analyze the optical limiting effect of copper nanoparticles. A theoretical model is presented and shows that at high laser light intensity, nonlinear light scattering occurs. By analyzing the experimental data with the presented model, the values of optical nonlinearities of copper particles were found to be $n_2 = 0.8 \times 10^{-19} m^2 w^{-1}$ and $\gamma = 1.46 \times 10^{-13} m/W$, respectively. Our work confirmed that Cu nanoparticles show outstanding nonlinear optical features, which can cause the development of nonlinear optics.

Keywords: copper nanoparticles, Z-scan technique, nonlinear absorption, nonlinear refraction

1. Introduction

The nanoparticles are increasingly used in the fields of biology [1, 2] and medicine [3, 4]. Additionally, materials with optical nonlinearities are crucial components to develop advanced photonic circuits [5] and optical communications in the future [6, 7]. Because of their controllable nonlinear optical properties, nanomaterials are garnering increasing attention, particularly in the realm of photonic instruments [8–10]. We recently learned that temperature changes in and around metal nanoparticles can increase the nonlinear refraction of the third order in the medium [11]. It has been proven that metal nanoparticles have positive impact on nonlinear optical response [12–14], making them an attractive option for nonlinear optical devices like optical limiters [15]. To prevent damage to human eyes and optical devices caused by high intensity laser beams, optical limiters are increasingly used in optical fields to ensure security. These systems strongly transmit low intensity laser light and increasingly reduce high intensity laser light. Research on optical limiters primarily revolves around discovering appropriate materials and identifying the corresponding mechanisms involved. Research shows that colloidal solutions of metal nanoparticles have high optical limiting.

Research has shown that metal nanoparticles like platinum, silver, and gold have larger nonlinear responses than their bulk metal counterparts [16, 17]. Nano-sized copper particles posse several benefits, including large optical nonlinearities, chemical stability, thermal stability, and impressive mechanical strength, which make them candidates for use in various fields such as superconductors, sensors, and electrochemistry. They are particularly useful for conductive coatings and biosensors. Additionally, Cu-NPs are effective in preventing skin photosensitivity [18]. Because the surface plasmon peak of Cu-NPs occurs at a wavelength of about 600 nm, these nanoparticles exhibit strong absorption of light rays in the visible region. Ryasnyansky et al. [19] conducted a research on optical nonlinearities of Cu nanoparticles. However, up to date, a thorough study of nonlinearities in Cu-NPs and presenting theoretical models is still blank yet.

There exist different techniques for producing metal nanoparticles, and some of them include chemical reduction, ultraviolet photochemistry, and laser ablation. Out of these, laser ablation stands out as the most efficient and straightforward approach for generating diverse nanoparticle types within a liquid medium [20–22]. It is also considered an effective method for making various types of nanoparticles, metals [23], semiconductors [24], and metal oxides [25]. The lack of vacuum equipment and chemicals, as well as the simplicity of the test arrangement, has made available a unique method for the fabrication of particles in nano dimensions. With this method, nanoparticles are created with very high purity and in any desired substrate. Surface contamination during metal-in-liquid laser quenching is reduced compared to chemical synthesis involving the decomposition salt of

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metals, because in the laser ablation method, particles are directly ablated from the surface of a pure metal in a net solvent.

In my research paper, we successfully created Cu nanoparticles using the laser ablation technique of a copper target in distilled water. To investigate the optical nonlinearities of the Cu nanoparticle suspended in water, we employed open aperture Z-scan and closed aperture Z-scan setup. To determine the absorption and nonlinear refraction of liquids, liquid solutions, and solids, Z-scan technology is a fast and efficient technique. It works by utilizing the self-lensing phenomenon to obtain the value and sign of nonlinear refraction of the samples. From the transmittance curve, the refraction coefficient and nonlinear absorption coefficient of the sample are determined [26]. By irradiating the Cu nanoparticles with laser rays with wavelength of 532 nm, we found that the origin of the nonlinearity created in the sample is nonlinear scattering, which is itself caused by nonlinear absorption process.

2. Experimental Procedure

Cu-NPs were produced by laser ablation method of very genuine Cu plate in deionized water utilizing a nanosecond pulsed laser. We performed laser ablation of copper by means of a Q-switched Nd: YAG laser that operates at a second-harmonic wavelength. The laser produced 15 ns (FWHM) pulses at 532 nm with a repetition rate of 1 Hz. We utilized a lens whose focal length was 45 cm to converge the laser ray on a $10 \times 10 \times 1$ mm^2 plate of copper situated inside a quartz cell with 10 mm thick containing deionized water. The laser pulse had a Gaussian spatial profile. The size of the beam waist was 300 μm and we set the laser fluence to 12 mJ/cm^2 for better copper laser ablation results. Laser ablation was done for 30 min. The concentration of the Cu nanoparticles was 3.58×10^{-4} mol/L. We used transmission electron microscopy (TEM) to determine the geometric shape of nanoparticles and their size distribution. We used a UV-Vis optical absorption spectrophotometer to verify the Cu nanoparticles.

The optical nonlinearities of the produced Cu nanoparticles determined by Z-Scan experiments. Experiments were performed with a laser beam with a wavelength of 532 nm. The experimental setup in this work is shown in Figure 1. A laser beam is passed through an attenuator and beam splitter before being irradiated on a sample with a 50 cm lens. In the focal region, the spot size was 150 μm. Two energy detectors used to measure the amount of the incident and transmitted beams energy. Additionally, an aperture with the ability to change its diameter was located before the output energy detector to distinguish nonlinear scattering from nonlinear absorption effects. We were able to move the sample-containing cell through the focusing area by utilizing a translation

machine that operates along the propagation axis (Z-axis). The cell had a thickness of 5 mm. At $z = 0$, the focal point, the sample receives the most laser intensity and decreased on both sides of the focal area gradually.
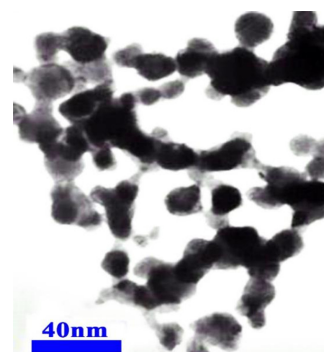
3. Results and Discussion

We have found that the UV-Vis absorption spectrum of the Cu-NPs produced by laser ablation method is shown in Figure 2. It is evident from the figure that the Cu-NPs have an absorption peak known as surface plasmon peak. This peak occurred at approximately 619 nm wavelength, which indicates the presence of sphere-shaped nanoparticles. This result agrees with the results reported in previous research [27–29].

Figure 2
Absorption spectrum of the Cu nanoparticle suspension
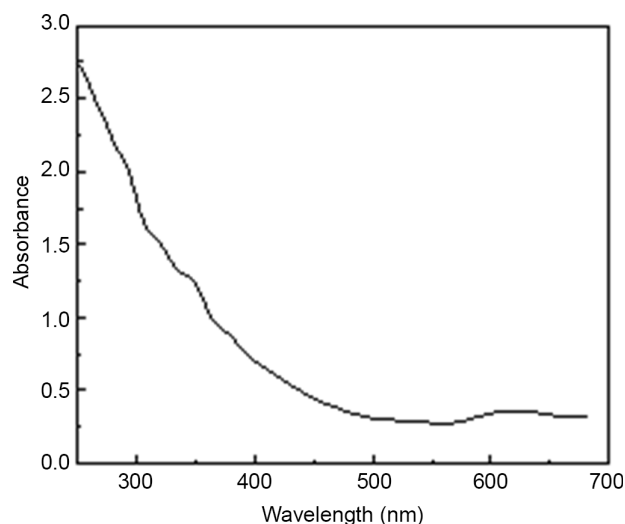
Furthermore, a shape of nanoparticles and their size were determined by TEM, as seen in Figure 3. It was discovered that the diameter of nanoparticles is about 40 nm with a standard deviation of 9 nm. Nanoparticles, shape is spherical and they were very stable for 1–2 weeks.

Figure 1
The Z-scan optical setup

Figure 3
TEM image of Cu nanoparticle soluble in water
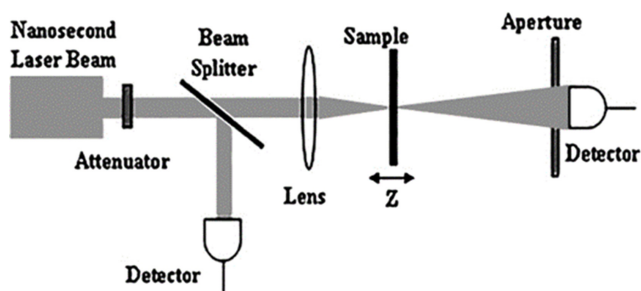
Figure 4
Optical limiting performance for the copper nanoparticles

Figure 5
Z-scan measurement with open aperture
of Cu-NPs in deionized water
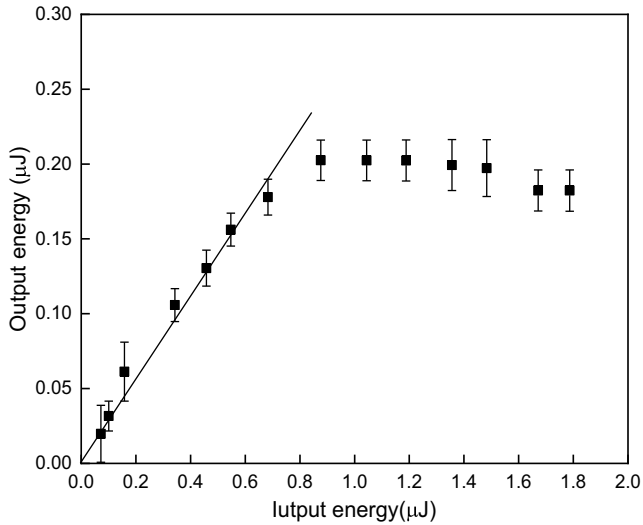
We have looked into the optical limitation of Cu-NPs dispersed in deionized water employing laser pulses. The wavelength of the laser pulse is 532 nm. Figure 4 illustrates the optical limiting performance of the Cu nanoparticles, and the diameter of the aperture of 4 mm was used before the output detector. It was observed that the optical limiting curve is linear up to energies of about 0.7 μJ. However, when the input laser energy increases from 0.7 to 2 μJ, the curve deviates from linearity. When investigating the optical limiting behavior of distilled water, it did not show any changes for input laser pulse energies from 0.7 to 2 μJ. In the optical limiting curve, the slope of the curve for distilled water was 1.0, whereas the slope of the line curve for copper nanoparticles is about 0.5. The mechanisms responsible for the limiting effects can be classified into three types of nonlinear processes, which include absorption, refraction, and nonlinear scattering. It seems that the nonlinear scattering causes the optical limitation of the Cu-NPs, which resulted in further reduction of output energy.

We have looked into the Z-scan experimental results with open aperture of Cu nanoparticles suspension in deionized water, and Figure 5 presents the data. It was observed that upon excitation intensity of 90 Mw/cm², the reverse saturable absorption was dominant. The solid curve shows the experimental data fitted with the theoretical model for nonlinear adsorption.

As soon as the laser beam is irradiated toward the sample, the laser light is absorbed by the sample in a nonlinear process and the temperature of the nanoparticles increases. Increase in temperature then creates the centers of the scattering [30]. A theoretical model has been proposed to investigate the nonlinear phenomenon occurring in Cu-NPs, Figure 5. It appears that the laser light absorbed by nanoparticles induces a nonlinear scattering effect. It is believed that when nanoparticles absorb laser light energy, the resulting increase in temperature changes their nonlinear refractive index, which creates scattering centers. The governing relations for the absorption process in the *z* direction (propagation direction) are given as:

$$\frac{dI}{dz} = -\alpha I - \beta(I)I - \gamma I^2 \tag{1}$$
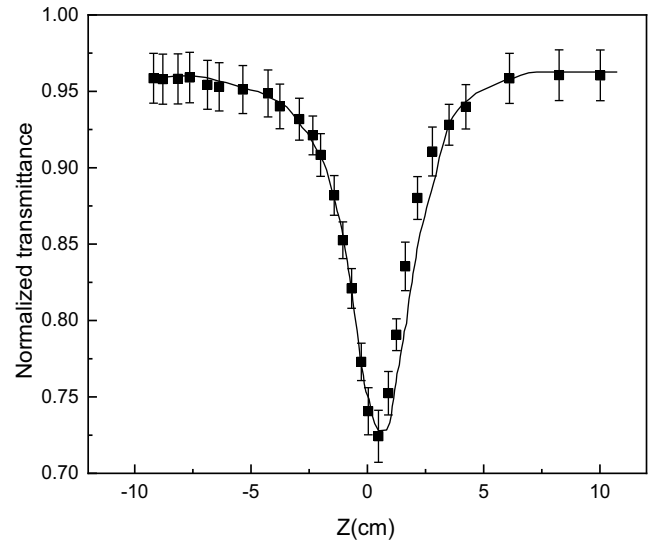
$$\frac{dT}{dt} = \frac{\gamma I^2}{\rho C_p} \tag{2}$$

where γ is defined as the nonlinear absorption coefficient,) the scattering coefficient is $\beta(I$, *I* is the input laser intensity, *T* is defined the temperature, the density is ρ, and C_p is defined the specific heat of Cu nanoparticles. The scattering coefficient is obtained using the Rayleigh–Gans equations [31, 32]:

$$\beta(I) = g_s[\Delta n_L + \Delta n_{NL}]^2 = g_s[\Delta n_L^2 + \Delta n_{NL}^2 + 2\Delta n_L \Delta n_{NL}] \tag{3}$$

where g_s is related to the diameter, geometric shape, and volume fraction of nanoparticles and is independent of laser intensity. Δn_L, Δn_{NL}, respectively, show the difference between the linear refraction coefficient and the nonlinear refraction coefficient of nanoparticles and the environment.

Refractive index changes are given by the following equation [33]:

$$\Delta n_{NL} = \left(\frac{dn}{dT}\right)\Delta T \tag{4}$$

where $\frac{dn}{dT}$ is defined as thermo-optic coefficient. By putting Equation (4) into Equation (3), we arrive at the following equation:
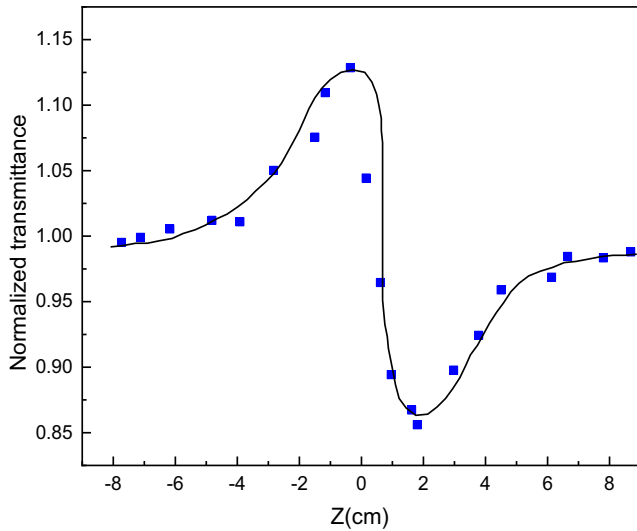
$$\beta(I) = g_s\left[\Delta n_L^2 + \left(\frac{dn}{dT}\right)^2(\Delta T)^2 + 2\Delta n_L\left(\frac{dn}{dT}\right)\Delta T\right] \tag{5}$$

If we assume that the temperature remains constant during laser pulse width, then Equation (2) is:

$$\Delta T \approx \frac{\gamma I^2 \tau}{\rho C_p} \tag{6}$$

where τ is the laser pulse width.

Figure 6
Z-scan measurement with closed aperture of Cu-NPs in deionized water

Substituting Equation (6) into Equation (4), we have:

$$\Delta n_{NL} = \left(\frac{dn}{dT}\right)\frac{\gamma I^2 \tau}{\rho_p} \tag{7}$$

Using Equation (7) into Equation (5), we have:

$$\beta(I) = g_s\left[\Delta n_L^2 + \left(\frac{dn}{dT}\right)^2\left(\frac{\gamma \tau I^2}{\rho C_p}\right)^2 + 2\Delta n_L\left(\frac{dn}{dT}\right)\frac{\gamma I^2 \tau}{\rho C_p}\right] \tag{8}$$

Since $\frac{dn}{dT}$ is very small, $\left(\frac{dn}{dT}\right)^2$ can be neglected. By defining $\alpha_s = g_s(\Delta n_L)^2$ and $\beta_s = 2g_s\Delta n_L\frac{\gamma \tau}{\rho C_p}\left(\frac{dn}{dT}\right)$ as linear and nonlinear scattering coefficients, respectively, and substituting Equation (8) into Equation (1), we have:

$$\frac{dI}{dz} = -\alpha I - \alpha_s I - \gamma I^2 - \beta_s I^3 \tag{9}$$

According to the presented theoretical model, Equation (9) was solved numerically for the primary Gaussian pulse. The extracted fitting parameters, including the linear and nonlinear absorption coefficients ($\alpha = 0.15$ cm^{-1}, $\gamma = 1.46 \times 10^{-13}$ m/W, respectively) and linear and nonlinear scattering coefficients ($\alpha_S = 0.85$ cm^{-1} and $\beta_s = 5.1 \times 10^{-18}$ cm^3/W^2, respectively), were obtained. Figure 5 shows that the experimental data align well with the theoretical model presented. It seems that the nonlinear scattering created in copper nanoparticles by nonlinear absorption is the main mechanism of their optical limitation when irradiated by laser pulses with a wavelength of nanoseconds.

We conducted a measurement of the nonlinear refraction of Cu-NPs using the closed aperture Z-scan method. The normalized transmission of the Z-scan measurements of the Cu-NPs is shown in Figure 6. We observed that the transmittance changes significantly near the focal plane ($z = 0$), while it remains relatively stable away from the beam waist. This results in strong nonlinearities due to the high energy density at the beam focus. Additionally, in our experiments, it was seen that when the sample is moved to positions (z) away from the focal plane (to the left of the focal point), the intensity of the beam is low and the visibly nonlinear refraction process does not occur in the sample, so the transmittance remains relatively stable. However, when the sample approaches the focal plane, the intensity of the laser beam on the sample increases and as a result nonlinear refraction occurs. The negative nonlinear refractive index of the sample causes the beam to diverge before it reaches the focal plane, resulting in the beam narrowing on the aperture and an increase in transmittance. As the sample continues to move toward the right side of the focal plane, the self-divergence of the beam causes the divergence to increase, leading to a wider beam across the aperture and a decrease in transmittance. The Z-scan experiment is considered complete when the sample moves away from the focus and the beam axis becomes linear again due to decreased beam intensity. The presence of a peak in transmittance before the focal point and a valley after the focal point in the transmittance curve indicates that the sample has a negative nonlinear refractive index.

The nonlinear refractive index n_2 was fitted using the following formula [34]:

$$T_N = 1 + \frac{4x}{(x^2 + 9)(x^2 + 1)}\Delta\phi_0 - \frac{2(x^2 + 3)}{(x^2 + 9)(x^2 + 1)}\Delta\psi \tag{10}$$

We were able to calculate the nonlinear refractive index to be approximately $0.8 \times 10^{-15} cm^2 w^{-1}$ by fitting the experimental data with Equation (10). This was done using the following parameters: $x = z/z_0$, $z_0 = 0.5$ kw$_0^2$ is defined as the Rayleigh length, $\Delta\phi_0 = kn_2I_0L_{eff}$, $\Delta\psi = \gamma I_0 L_{eff}/2$, $k = 2\pi/\lambda$ as the wave number, w_0 as the waist radius of the beam at focal point, I_0 as the intensity of the laser beam at the focal plane of the focus lens, n_2 as the nonlinear refractive index, γ as the nonlinear absorption coefficient, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ as the effective length of the nonlinear medium, L as the thickness of the sample, and α as the linear absorption coefficient of the sample. This suggests that Cu nanoparticles have a large nonlinear refraction, making it a promising candidate for use as a nonlinear nanomaterial. Table 1 compares the optical nonlinearities of copper nanoparticles.

Table 1
Comparison of the optical nonlinearities of Cu-NPs

Sample	n_2 (m^2/W)	γ (m/W)	Reference
Cu nanoparticles in distilled water	1.52×10^{-15}	3.5×10^{-13}	Boltaev et al. [35]
Cu nanoparticles in indium tin oxide matrix	5.18×10^{-12}	3.45×10^{-5}	Ryasnyansky et al. [19]

4. Conclusion

We conducted an experimental investigation on the optical nonlinearities of Cu nanoparticles and discovered that Z-scan measurements with open aperture indicate strong nonlinear absorption. The nanoparticle solution exhibited a robust optical limiting performance when subjected to nanosecond laser rays with wavelength of 532 nm. Based on our findings, the optical limitation of Cu nanoparticles is because of nonlinear scattering. Our experimental data and theoretical analysis of nonlinear scattering are in excellent agreement, providing insightful conclusions about the system we studied. The Z-scan test with closed aperture further revealed a large nonlinear refraction of Cu nanoparticles, indicating its potential as a new nonlinear nanomaterial.

Ethical Statement

This study does not contain any studies with human or animal subjects performed by any of the authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest to this work.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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