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RESEARCH PAPER

Studying Optical Nonlinearities of Copper Oxide Nanoellipses Using the Z-scan technique

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Abstract

We recently read about copper oxide nanoellipses and their potential applications in various fields. The researchers produced these nanoellipses using a laser ablation method of a pure copper sheet in distilled water and investigated their third-order optical nonlinearities by means of the typical z-scan technique using a Ti:S laser with a wavelength of 800 nm at 1µm. Open aperture z-scan experiments showed that copper oxide nanoellipses exhibit saturation absorption and reverse saturation absorption with increasing laser intensity. They also have optical limiting performance. Additionally, the researchers used the closed aperture z-scan experiment to investigate the nonlinear refraction properties of the copper oxide nanoellipses which was found to be positive. Overall, our work confirms the outstanding nonlinear optical properties of copper oxide nanoellipses and suggests their potential use in photonics and nonlinear optical devices.

1. Introduction

Today, nonlinear optical materials are widely used in various fields such as photonic circuits [1] and optical communications [2, 3]. Therefore, the finding of these materials has received much attention and research. Recently, the demand for nonlinear optical materials has been increasing to advance higher performance applications. In particular, atomic-thick 2D materials exhibit many prominent photoelectronic properties such as broad-band optical absorption [4], large optical nonlinearities [5, 6], which gives them the extraordinary ability to be nonlinear optical materials. Typically, these two-dimensional samples are nano-sized and have a large surface area [7, 8], which increase the strength, performance of optical and electrical devices [9].

Tran et al. [7] and Zhang et al. [10] have reported that transition metal oxides exhibit stronger nonlinear optical properties than other two-dimensional samples. Copper oxide in nano sizes (Cu_xO), in the form of copper oxide (CuO) [11] and copper oxide (Cu_2O) [12] have been researched more due to their unique nonlinear optical behavior compared to other transition metal oxide nanomaterials.

Copper oxide nanomaterials are used in various fields such as sensors, superconductors, and optoelectronics due to their superior optical, thermal and electrical properties. These nanomaterials are very popular because of their unique properties such as thermochemical stability [13], significant heat capacity [14], and remarkable optical nonlinearities. In fact, CuO is a p-type semiconductor that has a crystalline structure. Rakhshani et al [15] have measured the band gap of CuO that is about 1.2 eV, which ensures that the optical absorption of CuO occurs in the near-infrared (NIR) range. Ryasnyansky et al [16] measured the optical nonlinearities of copper nanoparticles located in the tin oxide matrix. The optical nonlinearities of nanoparticles of the Cu2S were also studied by Hamanaka et al [17]. They observed that the nonlinear refraction increases near the surface plasmon wavelength. However, to date, the optical nonlinear properties in CuO have not yet been fully explored, and the application of copper oxide nanomaterials for ultrafast modulation in the near-infrared region is an essential requirement. The aim of our research is to show that copper oxide nanoparticles show large optical nonlinearities under 55 femtosecond laser pulses.

In this article, CuO nanoellipses were synthesized using the laser ablation method [18] of pure copper plate in distilled water. Using open (OA) and closed (CA) aperture z-scan experiments, the nonlinear optical behaviors of CuO nanoellipses fabriceted under intracellular laser irradiation of 1 mm thick quartz were investigated. A variety of nonlinear optical characteristics appear with increasing intensity of the incident laser.

2. Fabrication of copper oxide nanoellipses in distilled water

We fabricated copper oxide nanoellipses using the laser ablation method of a piece of copper metal in distilled water. We used the Q-switched Nd:YAG laser at the base wavelength to ablation copper. The laser produced 18 nanosecond pulses (FWHM) with a wavelength of 1064 nm and a repetition rate of 1 Hz. The laser beam was irradiated on the copper surface with a lens with a focal distance of 50 cm. The sample was placed in a 10 mm thick quartz cell. The duration of the laser ablation was 30 minutes and the intensity of the laser beam on the sample was 100 J/cm^2. The volume fraction of produced copper nanoparticles was estimated as .Transmission electron microscopy (TEM) was used to confirm the formation of copper nanoparticles. Using a UV-Vis optical absorption spectrophotometer, the optical absorption of produced copper nanoparticles was analyzed. By taking the UV-Vis absorption spectrum in consecutive days after the production of the solution, its stability was investigated. It was found that the oxidation of the solution occurred during the laser ablation. We monitored the stability of CuO nanoellipses during optical nonlinearity experiments and determined the shape of copper nanoparticles dissolved in water one day after laser ablation. Figure 1 shows the UV-Vis absorption spectrum of nanoparticles. It can be seen that the nanoellipses have a surface plasmon absorption (SPA) peak equal to 300 nm, which is characteristic of these nanoellipses in distilled water.

With the help of transmission electron microscope, the shape and size of nanoellipses were studied. Figure 2 shows the image obtained by the transmission electron microscope of CuO nanoellipses in water. The formation of oval nanoparticles was seen. The width of particles was about 130-170 nm and their length of 200-230 nm. Based on theory "bottom-up" [19], it is possible to understand how copper nanoellipses are formed. According to this theory, aggregation creates single crystal copper oxide nanoparticles. We saw that during the time that copper nanoparticles are oxidized in water, aggregation occurs and tiny single crystal structures are seen.

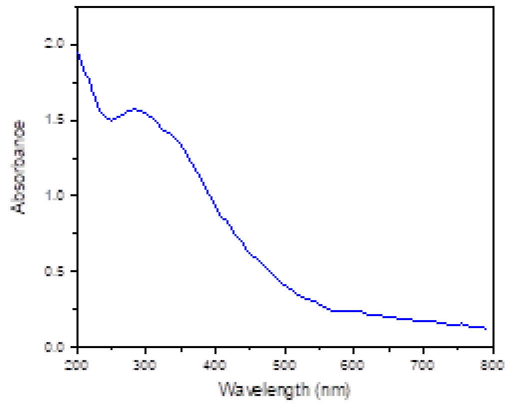

Fig. 1. Absorption spectrum of CuO nanoellipses.

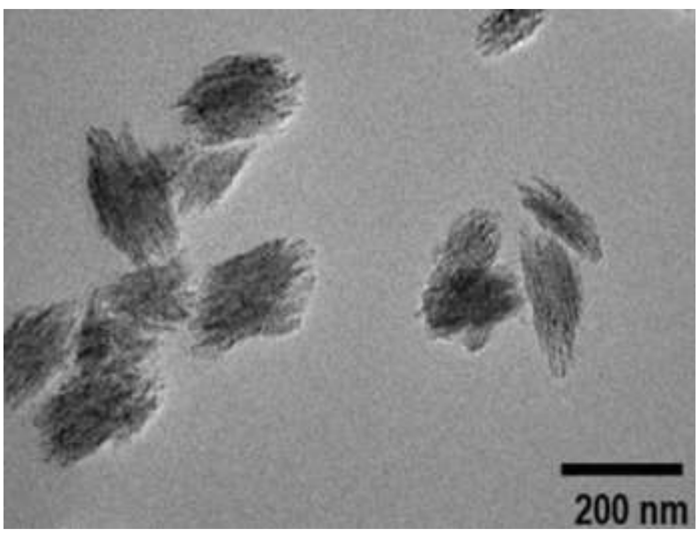

Fig. 2. TEM image of CuO nanoellipses dissolved in water.

3. Nonlinear optical properties

Z scan technique was used to measure optical nonlinearities of copper oxide nanoellipses. The laser used was a Ti:S laser with a wavelength of 800 nm, which produced pulses of 55 femtoseconds. Figure 3 shows the setup of the Z-scan experiment. A beam splitter splits the laser light into two beams, one beam as a reference beam and another to excite the sample. The detector directly absorbs the reference beam, but the other beam passes through a convex lens and is then irradiated onto the sample. The focal length of the lens was 100 mm. A two-channel power meter controlled the power of the incident laser and the transmitted laser. 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 5mm. At , the focal point, the sample receives the most laser intensity and decreased on both sides of the focal area gradually. Z-scan experiments were performed on the bulk material and no optical nonlinearities appeared. Therefore, the observed optical nonlinearities are only caused by copper oxide nanoellipses.

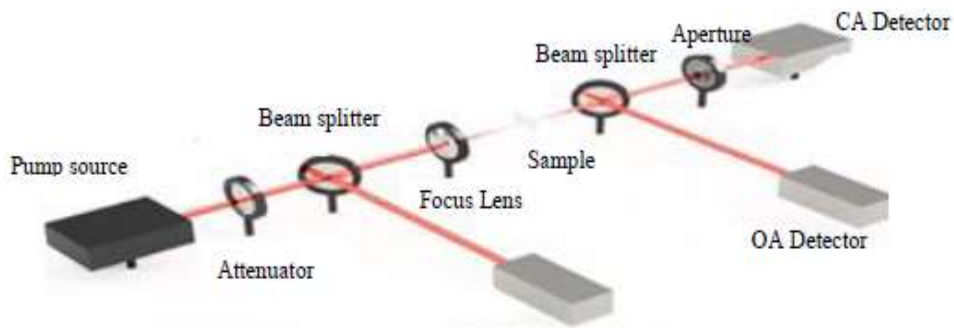

Fig. 3. A Z-scan setup was used to characterize the nonlinear optical properties of the sample.

3.1. Nonlinear saturable absorption (SA)

First, we performed open aperture Z-scan experiments to investigate the nonlinear saturable absorption of copper oxide nanoellipses. It was found that under laser irradiation with low intensities, nanoellipses show nonlinear saturable absorption. Figure 4 shows that when the sample approaches the focus (z=0), the transmittance increases from it.

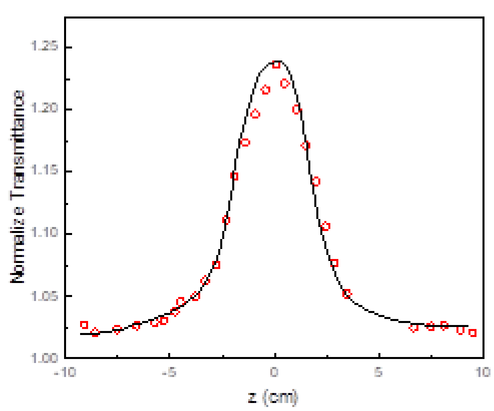

Fig. 4. Nonlinear optical absorption response of open aperture Z-scan CuO nanoellipses.

As it is clear from the figure, the nanoellipses are able to repress the laser with higher intensities to lower intensities until they were bleached. In the bleaching process, electrons are transferred from the valence band to the conduction band under powerful laser radiation (if the intensity of the incident beam on the material is too high, then the absorption coefficient tends to zero quickly. In this case, the beam will pass through the material even if the material be a good absorber of a low-intensity beam. This effect is known as bleaching. When bleaching occurs, a small fraction of the beam edges are absorbed to provide the energy needed to produce bleaching of the material in response to that wavelength.When the electrons of the valence band are placed in all states in the conduction band, the transition between the two bands stops and saturable absorption occurs [20]. In order to interpret the obtained experimental data and determine the nonlinear absorption coefficient, we fitted the transmittance curve in Figure 4 with the following formulas [22]:

$$T = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{1.5}}, m \in N \qquad q_0(z,0) = \frac{\beta_{eff} L_{eff} I_0}{\left(1+z^2/z_0^2\right)} \qquad (1)$$

$$L_{eff} = (1-e^{L\alpha})/\alpha$$

where β_{eff} is defined as the nonlinear absorption coefficient. L_{eff} is the effective length of the sample, α and L are the linear absorption coefficient and the thickness of the sample, respectively. The diffraction length of the beam is determined by z_0, and I_0 is the intensity of the beam at $z=0$.We fitted the experimental data with the above equations. The magnitude of β_{eff} was $-0.87 cm/MW$. This value for β_{eff} shows that copper oxide nanoellipses can be used for near-infrared modulation and as a nonlinear optical switch [23].

3.2. Nonlinear refractive index

We conducted a measurement of the nonlinear refraction of the CuO nanoellipses using the closed aperture Z-scan method. The normalized transmission of the Z-scan measurements of the CuO nanoellipses is shown in Figure 5. We observed that the transmittance changes significantly near the focal plane (z = 0), while it remains relatively stable away from the focal plane. This results in strong nonlinearities due to the high energy density at the point focus. In our experiments, the sample was moved along the z-axis around the focal plane of the lens, and for each z-location, the light transmittance from the sample was recorded. Different intensities were received by sample in different places, as a result, the optical Kerr effect induces self-focusing or self-defocusing in the sample. This means that nanoellipses act like a lens whose focal length depends on the intensity of the beam. Depending on whether the nonlinear refractive index of the nanoparticles is positive or negative, they converge or diverge the beam. The presence of a valley in transmittance before the focal point and a peak after the focal point in the transmittance curve indicates that the sample has a positive nonlinear refractive index. In Figure 5, the full curve is obtained by fitting the experimental data with the following equation [24]:

$$T = 1 + \Delta\varphi_0 \frac{4\left(z/z_0\right)}{\left(1+\left(z/z_0\right)^2\right)\left(9+\left(z/z_0\right)^2\right)} \quad (2)$$

$$\Delta\varphi_0 = k n_2 I_0 L$$

where $\Delta\varphi_0$ is defined nonlinear phase shift, k is known as the wave number in vacuum, L, and n_2 are sample thickness, and nonlinear refractive index, respectively. The magnitude of n_2 was calculated as $1.23\times10^{-15}\ cm^2/W$ for CuO nanoellipses.

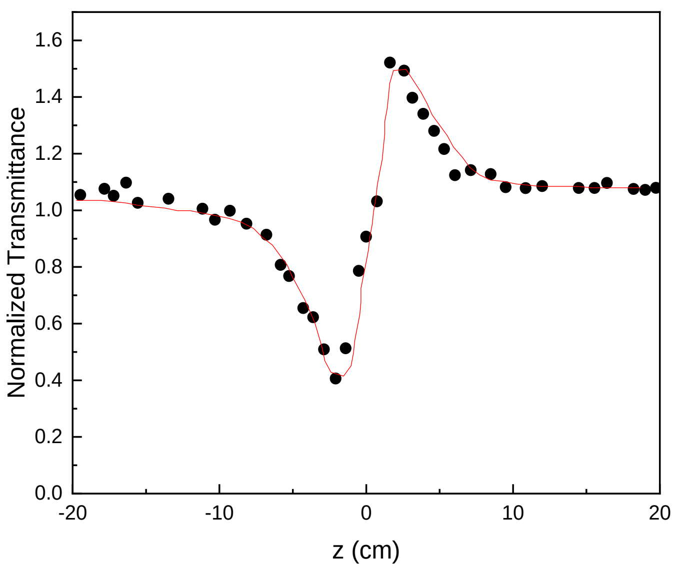

Fig. 5. Experimental results of Z-scan closed aperture of CuO nanoellipses

In Table 1, optical nonlinearities of CuO nanoellipses are compared with other nanomaterials. As it is known, CuO nanoellipses show a larger nonlinear absorption. The nonlinear absorption of goat along with their thermal stability can introduce CuO nanoellipses as candidates for application in nonlinear optical devices.

Table 1. Comparison of nonlinear optical properties of different nanomaterials.

Sample	β_{eff} (cm/W)	$n_2\,(cm^2/W)$	Ref.
ZnO nanoparticles	4.6×10^{-11}	1.6×10^{-15}	[29]
Ag@ZnO core-shell nanostructures	-	-1.66×10^{-15}	[30]
ZIF-67	-8.5×10^{-10}	-0.93×10^{-15}	[21]
CuO nanoellipses	-8.7×10^{-6}	1.23×10^{-15}	This work

3.3. Optical limitation

When the on-axis laser beam intensity is increased to about 60 MW/cm^2, the transmittance of the light from the sample decreases. This means that reverse saturation absorption has occurred in the sample [25]. In Figure 6(a), there are still two maxima on the sides of the center, which indicates the saturable absorption behavior of the sample [26]. But when the intensity of the incident beam laser on the sample reached about 90 MW/cm^2, the transmittance of the light decreased more than the sample at z = 0, and the transmittance maxima on the sides of the center disappeared (Figure 6(b)).

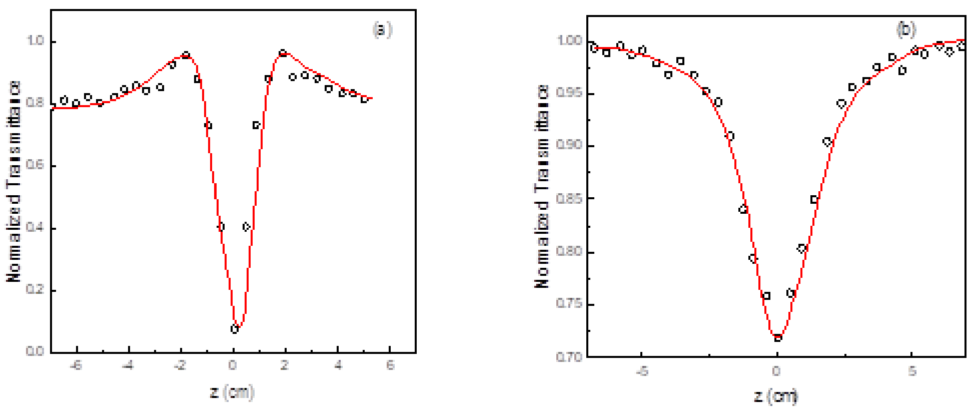

Fig. 6. Reverse saturation absorption of CuO nanoellipses for incident laser intensity a) 60 MW/cm^2 and b) 90 MW/cm^2.

With the increase of laser intensity, gradually reverse saturation absorption became dominant nonlinear absorption in the sample, indicating optical limiting behavior. By fitting the experimental data with the following formula, the value of the reverse saturable absorption coefficient was obtained [27]:

$$T=\left[1-\frac{\alpha L I_S}{I_S+I_0/\left(1+z^2/z_0^2\right)}-\beta L I_0/\left(1+z^2/z_0^2\right)\right]/\left(1-\alpha L\right) \qquad (3)$$

From the experimental data, the value of I_S, 3 and the value of β (reverse saturable absorption coefficient) under laser light intensities of 60 and 90 MW/cm^2 were determined to be 1.1 and 1.58 cm/MW, respectively. It was found that the reverse saturation absorption coefficient strongly depends on the laser intensity. A similar optical limiting behavior appeared in copper oxide nanocrystalline films [28].

4. Conclusions

In this work, we investigated the nonlinear absorption of copper oxide nanoellipses by using the open aperture Z-scan technique. We observed that at low intensities of the laser, saturable absorption occurs in the sample, but with the increase in the intensity of the incident laser beam, the reverse saturable absorption dominates. In addition, we also investigated the nonlinear refraction of copper oxide nanoellipses with the help of closed aperture Z-scan technology. From the experimental data, a large nonlinear refractive index value was estimated for the sample, which can introduce it as a useful nonlinear nanomaterial. Our research work calls for further study in the field of optical nonlinearities of copper oxide and other transition metal oxides due to their many applications in optoelectronics and photonics.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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