In the present study, gold nanoparticles were synthesized in various polymer solutions by means of employing laser ablation technique at the same ablation time. Specifically, gold nanoparticles were synthesized in polyethylene glycol and chitosan solutions, in order to compare the effects of the liquid media which served as stabilizers for particle size and volume fraction of nanoparticles. In addition, this experiment was repeated in distilled water for reference purposes. As the findings indicated, the particle size which was obtained in polyethylene glycol was about 7.49 nm, that is, smaller than those of chitosan solution and distilled water, respectively. In contrast, it was observed that the volume fraction of gold nanoparticles increased in polyethylene glycol in comparison with the other media which indicated an effect on the formation of NPs. On the other hand, Z-scan technique was employed to measure the nonlinear refractive index and nonlinear absorption coefficient of nanofluids containing gold nanoparticles. Consequently, the nonlinear properties of nanofluids pointed to a significant contribution with the number of nanoparticles observed in fluids and both optical nonlinear parameters were observed to increase by means of a prior increase in the volume fraction of Au-NPs in polyethylene glycol solution.

1. Introduction

A shift from the existing chemical methods into Laser ablation in liquid phase (LALP) to synthesize nanoparticles (NPs) has over the years been observed owing mainly to its environmental-friendliness, contamination-free, and nonhazardous. Among various NPs which are widely available, gold nanoparticles (Au-NPs) drew particular attention among scholars owing to its wide range of applications such as sensors [1], electronics [2], medical diagnoses [3], and therapeutic agent delivery [4]. In this regard, it has to be noted that the response of the NPs to the interaction of light is dependent on the size of the particles [5]. A review of related literature clearly indicates variations observed in methods employed to prepare Au-NPs, for instance, the chemical methods [6, 7], sonochemical [8], microwave technique [9], Green synthesis of Au-NPs using plane leaf extract [10], organic solvents [11], nonorganic solvents [12], graphene oxide [13] by means of LALP, and ion implantation [14]. Moreover, Au-NPs are very interesting when they are deposited on the ITO substrates [15], for instance, particular interest for the photoinduced nonlinear optics determined by interfaces between the conductivity of electrodes and the charge density distribution [16].

It has been reported that nonlinear optical properties of Au-NPs by means of electron beam deposition have been studied by employing Z-scan technique [17]. It is worth highlighting that Z-scan technique is a simple and accurate technique which can be useful in determining the nonlinear (NL) properties. It can also be observed that, in this technique, the laser beam goes through the focal point of the beam from NL medium and changes in its transmittance, which in turn may cause the nonlinear refractive (NLR) and nonlinear absorption (NLA) which are measured by both the close
aperture and open aperture, respectively. The NLR index of high NL aggregate film which is based on self-assemble Au-NPs is reportedly measured by Z-scan technique [18]. Moreover, the NLR index of the colloidal Au-NPs under the continuous wave illumination is reportedly investigated by means of employing the z-scan technique [19].

As in the case of the present study, the focus was on looking into synthesizing the Au-NPs in polyethylene glycol [20] and chitosan [21] solutions by employing LALP technique in order to measure the effect of liquid media on both the size and formation of NPs. The LALP is considered as a green method in comparison with chemical method that has been used to synthesis gold nanoparticle. Moreover, the novelty of present study is using polymer solution instead of distilled water to decrease the size of Au-NPs. The focus then shifted to investigating the effect on optical NL properties of nanofluids containing Au-NPs. The samples which were prepared for the present study featured a UV-Vis spectrometer (UV-1650 PC, Shimadzu) with 1cm optical path cell to confirm the Au-NPs peak absorption, TEM (Hitachi H-7100) at 120kV accelerating voltages for NPs’ morphological information, and atomic absorption spectrometer (AAS, S Series) which may serve to measure the mass of Au-NPs in solution. Also, Z-scan technique was used to measure NL optical properties, respectively.

2. Experimental Details

2.1. Fabrication of Au-NPs Using Laser Ablation Technique. In order to produce the Au-NP, a gold plate (i.e., Sigma-Aldrich, 99.99% purity) that was initially washed by means of using ultrasonic bath for an estimated 30 minutes was placed in a cubic cell including a 20 mL of solution. At this stage, both the chitosan and polyethylene glycol (PEG) solution were used to serve as stabilizers. In this regard, an estimated 2 g of chitosan and 2 g of PEG powder were dissolved into 100 mL of water. The chitosan solution was prepared within an estimated one hour at 60°C and preparation PEG solution was also similarly conducted for one hour but at room temperature.

The Q switched Nd:YAG pulse laser (SL400/SL800 system) with 532 nm wavelength, 10 Hz repetition rate, and 10 ns duration, respectively, was used for ablation to produce Au-NPs from the target. The laser output power 35 mJ/pulse was measured by the optical power detector (Nova II) [22]. The laser beam was focused on the plate by means of using a lens with 25 cm focal lengths. The ablation was carried out at room temperature for an estimated 15 minutes and, in the course of ablating the solution, it was magnetically stirred to ensure they are well dispersed. Figure 1(a), shows the schematic diagram of laser ablation set-up.

Here, volume fraction was calculated through a simple relationship:

\[ V = \frac{V_s}{V_s + V_L} \]

where \( V_L \) is the liquid volume, \( V_s = m/\rho \) is the volume of Au particles, \( \rho \) is the Au density, and \( m \) is the Au particle mass dispersed in solution [23].

2.2. Nonlinear Properties of Au-NPs Using Z-Scan Technique. Z-scan set-up in this context was considered to determine the NLR index and the NLA coefficient of nanofluids. The schematic diagram of Z-scan experimental set-up is shown in Figure 1(b). It has to be noted that the experiment was conducted at room temperature with a CW green laser diode working at 532 nm wavelength (SDL-532-150T). The beam was focused at a small spot using a convex lens with a measurement of 10 cm in focal length and the sample was then moved along the z-axis by microstepping controller (BSC101), run by a Lab View program. The power output of the laser beam at the focal point (40 mW) was measured by power meter (Newport 193-6). The light transmitted in the far field passed through the aperture (i.e., aperture size 2 mm) and the beam intensity was recorded by a silicon photo detector (i.e., Newport 918D-SL-OD3). A quartz optical cell containing the sample solution was moved across the focal area along the direction of z-axis to extract the NLR index, and the NLA coefficient was measured in line with the closed aperture and open aperture Z-scan experiment.
2.2.1. Closed Aperture. The NLR index \( n_2 \) can be computed from the fitting of normalized transmittance of the experimental data along with the theoretical transmittance curve of closed aperture in accordance with (2) in the following:

\[
\Delta T(Z, \Delta \phi) = 1 - \frac{4\Delta \phi_0 x}{(x^2 + 1)(x^2 + 9)},
\]

(2)

where \( \Delta \phi_0 \) is the axis phase change at the focus point, \( x = Z/Z_0 \), \( x \) is a normalized distance on the \( z \)-axis, and \( n_2 \) is related to phase change [24, 25].

\[
n_2 = \frac{\Delta \phi_0}{k I_0 L_{\text{eff}}},
\]

(3)

where \( k \) is a wave vector, \( I_0 \) is the beam intensity at focus point, and \( S \) is the aperture linear transmittance. \( L_{\text{eff}} \) is the effective thickness of the sample that is obtained by means of the following equation, where \( \alpha \) is the linear absorption coefficient and \( L \) represents the sample thickness (1 mm).

\[
L_{\text{eff}} = \frac{1 - \exp(-\alpha L)}{\alpha}
\]

(4)

2.2.2. Open Aperture. On the other hand, if the sample saturated absorption is observed as a consequence of increasing incident intensity, the transmission may in turn reach the maximum level in the focal region [26]. In this case, transmitted light is measured by means of a detector in the absence of an aperture and the measured quantity is the normalized transmittance which is provided by the equation in the following [27]:

\[
T = q_0^{-1}(z) \ln \left(1 + q_0(z)\right), \quad |q_0(z)| < 1,
\]

(5)

where \( q_0(z) \) is a parameter characterizing the strength of the nonlinearity that for Gaussian beam.

\[
q_0(z) = \beta I_0 L_{\text{eff}},
\]

(6)

where \( \beta \) is a NLA coefficient that is obtained by fitting the experimental data with theoretical data (see (5)).

3. Results and Discussion

3.1. Characterization of Au-NPs. Figure 2 indicates the UV-visible absorption spectra of Au-NPs prepared by LA in PEG, chitosan solution, and distilled water as references, respectively. The estimated peaks of 530–550 nm for all samples are related to the formation of Au-NPs [28, 29]. It is obvious that the maximum wavelength indicated a slightly blue shift from 550 nm to 524 nm from distilled water to the PEG solution, respectively. Such a shift, according to the Mie theory, is due to the size reduction of particles [30]. Another interesting point from UV-visible spectra is the increasing intensity of surface Plasmon resonance (SPR) observed in various media that clearly indicates that the intensity of SPR in PEG is relatively higher than other media. The intensity of surface plasmon may have a direct relationship with the density of particles contained in solutions. Referring to the scenario, it can be interpreted that the concentration of Au-NPs in PEG is slightly higher than that of chitosan solution and distilled water as well, which is confirmed by measuring volume fraction (see (1)) of NPs in solutions.

Thus, Figure 3 clearly illustrates that the volume fraction along with the intensity of absorption of Au-NPs in this context is highly dependent on liquid media which were used as stabilizers to synthesize NPs. Nevertheless, it is worth highlighting that both parameters observed significant reduction in distilled water in comparison with the polymer solutions.

The TEM images and mean diameter of particles for synthesized Au-NPs in various polymer solutions and distilled water are demonstrated in Figure 5. The small particle size gained from PEG is largely due to the TEM images. The
details of Au-NPs, namely, mean size, standard deviation, and volume fraction in all media are illustrated in Table 1. Moreover, the mean particles size, which is approved by UV-visible spectra is obtained and the blue shift showed that the particles diameter of Au-NPs in PEG were smaller than other media. Moreover, TEM images have also confirmed the approximately spherical shape of Au-NPs in solutions. Another noticeable point in TEM images was the dispersing NPs in solution which indicates that Au-NPs is well dispersed in PEG compared to chitosan solution and water.

Size reduction occurred due to the interaction between the liquid media of NPs after formation. NPs may be absorbed by solution because it is the key players in preventing NPs from agglomeration and growing. The mechanism of capping Au-NPs in PEG solution may be explained by hydroxyl groups [31], while, in chitosan solution, it occurred via hydroxyl groups and nitrogen atoms of amine groups [32], which were schematically indicated in Figure 4.

Figure 6 indicated the clear relationship of particle size with volume fraction and the absorbance intensity Au-NPs, which were prepared simultaneously with ablation time. Notably, decreasing the particle sizes in PEG solution yielded an increase in the fraction volume and, consequently, the absorbance intensity also increased due to the high viscosity and density of PEG solution compared to other media.

3.2. Optical Nonlinear Properties. The nonlinear properties of samples, namely, particle size and volume fraction of Au-NPs, were investigated in polymer solutions. Figure 7 shows the normalized transmittance of closed aperture of Z-scan experiment for Au-NPs in PEG and chitosan solutions. The particles’ sizes and fractions’ volume derived from Au-NPs in both media are itemized in Table 1. Asymmetric curves were observed due to the fact that the theoretical transmittance curves fitted well to the experimental data for samples in liquid phase containing gold NPs. Moreover, the normalized transmittance signal was obtained in accordance with the maximum peak value. It should be noted that the peak-valley shapes of the curves indicated the self-defocusing phenomena of Au-NPs. The results suggested that \( n_2 \) increased more in PEG solution rather than in the chitosan solution. \( n_2 \) Results obtained from (2) were negative, thus, confirming the occurrence of self-defocusing phenomenon [33, 34].

Figure 8 illustrates the NLA asymmetry curves of Au-NPs in PEG and chitosan solutions. Asymmetric samples were obtained owing to the laser beam heating, which created waves that passed through the quartz cell with 1 mm thickness inside the samples [35, 36]. The NLA coefficient, \( \beta \), was obtained from fitting the theoretical normalized transmittance data (see (4)) to the experimental open aperture data [37].

Table 2 indicates the optical nonlinear results of Au-NPs obtained in both media. It should be noted that the increasing volume fraction and decreasing particle size of NPs in PEG solution (i.e., demonstrated in Table 1) were reflected in the NLR index and NLA coefficient of NPs, in which they also increased compared to in chitosan solution. The results of optical NL properties obtained are listed in Table 2.

Thus, the nonlinear properties of nanofluids containing Au-NPs noticeably increased by increase of the concentration of NPs in polymer solutions and it depended on the size of Au-NPs as well [13]. Subsequently, Figure 9 presented the relationship of NLR index and NLA coefficient with particle size and volume fraction of Au-NPs in polymer solutions.

4. Conclusions

The nonlinear refractive index of gold nanofluid, which was prepared at different particle sizes in various polymer solutions has been successfully measured by means of a single beam Z-scan method. The measurement was carried out at room temperature using a CW green laser beam at 532 nm wavelength. Notably, the Au-NPs indicated a good nonlinear response. The sign of the nonlinear refractive index was negative indicating self-defocusing phenomenon and the magnitude was in the order of \( 10^{-7} \) cm\(^2\)/W. The nonlinear effect increased with the decrease of particles’ size in PEG solution at an estimated 7.49 nm. On the other hand, NLA coefficient increased together with the volume fraction’s increase of Au-NPs in PEG solution compared to that in the chitosan solution.

Competing Interests

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

Authors’ Contributions

The main idea for the experiment was thought up by Mojgan Tajdidzadeh. Experimental work and analysis of the experimental data was performed by Mojgan Tajdidzadeh and S. Shirzadi. The analysis of the experimental data was carried out by Azmi B. Zakaria and Zainal Abidin Talib. Mojgan Tajdidzadeh and Azmi B. Zakaria, A. S. Gene, and S. Shirzadi have participated in writing the manuscript.

Table 1: Mean diameter, standard deviation, and volume fraction of Au-NPs in polymer solution.

<table>
<thead>
<tr>
<th>Media</th>
<th>Mean diameter (nm)</th>
<th>Standard deviation (nm)</th>
<th>Volume fraction ( \times 10^{-7} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>7.49</td>
<td>1.91</td>
<td>6.3</td>
</tr>
<tr>
<td>Chitosan</td>
<td>10.33</td>
<td>2.42</td>
<td>0.58</td>
</tr>
<tr>
<td>Distilled water</td>
<td>20.76</td>
<td>4.83</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 2: NLR index and NLA coefficient of Au-NPs in PEG and chitosan solutions.

<table>
<thead>
<tr>
<th>Media</th>
<th>( \Delta \phi_0 ) ( \times 10^{-7} )</th>
<th>( n_2 ) (cm(^2)/W) ( \times 10^{-7} )</th>
<th>( \beta ) (cm/W) ( \times 10^{-7} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>-0.411</td>
<td>-8.2</td>
<td>1.48</td>
</tr>
<tr>
<td>Chitosan</td>
<td>-1.715</td>
<td>-3.4</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Figure 4: Schematic diagrams of capping Au-NPs: (a) chitosan solution and (b) PEG solution.
Figure 5: TEM images and their accompanying size distribution of Au-NPs in various media: (a) chitosan, (b) PEG, and (c) distilled water.
Figure 6: Relationship between volume fractions, particle size, and intensity of absorbance of Au-NPs in polymer solutions and distilled water.

Figure 7: Normalized transmittance curve of closed aperture $Z$-scan set-up for Au-NPs (a) chitosan and (b) PEG solution prepared at 15 min ablation time.

Figure 8: Normalized transmittance curve of open aperture $Z$-scan set-up of Au-NPs in (a) chitosan solution and (b) PEG solution.
Acknowledgments

The authors gratefully acknowledged the financial support for this work from the Fundamental Research Grant Scheme (FRGS) of Project no. 01-02-13-1345FR and IPS Putra Grant of Project no. GP-IPS/2014/943964.

References


Submit your manuscripts at https://www.hindawi.com