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Research Article

Green Fabrication of Copper Nanoparticles Dispersed in Walnut Oil Using Laser Ablation Technique

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Synthesis of copper nanoparticles was achieved by laser irradiation of copper plate in walnut oil. The copper plate was irradiated using Nd:YAG pulse laser at different ablation time from 5 to 50 minutes, and the prepared samples were characterized using analytical methods to find the optical absorption, morphology, particle size, and capping of copper nanoparticles with walnut oil. Consequently, the absorption peak appeared at about 615, 606, 588, 576, and 561 nm; and the nanoparticles formed in spherical shape in walnut oil. The particle size varied from 25 to 4.01 nm, and the tail of the carbonyl band capped the copper nanoparticles through the electron transfer from the carboxylic group to copper nanoparticles. The refractive indices of the nanofluid were measured using a surface plasmon resonance technique and changed from $1.4691 + 0.008i$ to $1.4682 + 0.043i$ as the volume fraction increased from 0.0257×10^{-5} to 1.26×10^{-5}. Consequently, the laser ablation method is environmentally sensitive (i.e., green) and thus is suitable for the fabrication of copper nanoparticles in walnut oil without any agent.

1. Introduction

Copper nanoparticles (Cu-NPs) have broad application in industry and medicine due to their physical and chemical properties [1–3]. The high electrical conductivity of Cu-NPs makes them suitable for applications such as modern electrical circuits, biosensors [4], and sintering additives [5]. Cu-NPs also have other uses including anti-inflammatory [6], antioxidative [7], and antiulcer [8] application. In addition, they have been used in medicine to prevent skin photosensitivity [9] and nanoprobes. Copper nanoparticles also include considerable localized surface plasmon resonance (LSPR) in the visible region and high surface-enhanced Raman scattering.

Many methods including solution phase [10], photochemical [11], sonochemical [12], and electrochemical synthesis [13] are used to prepare and disperse copper nanoparticles in various mediums. Laser ablation introduces a green method for fabricating Cu-NPs [14]. The preparation of Cu-NPs in water [15], dichloromethane [16], acetonitrile [16], chloroform [16], alcohol [16, 17], and coconut oil [14] using laser ablation has been reported in the literature.

Walnut oil contains oleic (18:1), linoleic (18:2), and linolenic (18:3) acids and palmitic acid (c16:1), while concentrations of other fatty acids such as myristic acid, palmitoleic acid, eicosenoic acid, and stearic acid are very low. However, walnut oil is rich in omega-3 fatty acids, vitamins B-1, B-2, and B-3, vitamin E, and niacin, and the LDL (bad cholesterol) ratio to HDL (good cholesterol) is lower than that with other oils; hence, it is healthier and more helpful than other oils in reducing the risk of coronary artery disease [18]. Walnut oil is used in cooking and skin care because the omega-3 fatty acids it contains have high permeation in human skin and have become popular ingredients in natural skin care products [19].

Copper and copper nanoparticle are the mineral for healthy skin and they sometimes are used in cream and skin care spray and lotion. Therefore, in this study, the Cu-NPs were prepared in walnut oil using laser ablation. The nanofluids are characterized using UV-visible spectrum, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), and atomic absorption spectroscopy (AAS) to obtain the optical absorption, particle size, morphology of nanoparticles, explanation of capping nanoparticles with walnut oil, and concentration of nanoparticles for different ablation times. Surface plasmon resonance (SPR) is an accurate method to obtain the real and imaginary parts of a refractive index. Hence, the refractive indices of walnut oil and nanofluids were measured using the SPR technique to investigate the amount of variation in the refractive index of nanofluids with different concentrations of Cu-NPs.

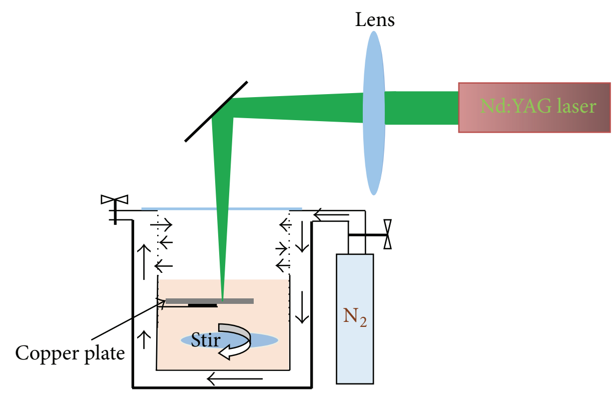

FIGURE 1: Laser ablation setup to prepare Cu-NPs in the walnut oil. The setup contains a Nd:YAG pulsed laser at wavelength 1064 nm, a lens (f = 300 mm), a stirrer, an insulator liquid tank, and N_2 gas. The dimensions of copper plate and fluid cell were 10 × 10 × 3 mm and 20 × 20 × 40 mm, respectively. The copper plate was ablated at different times such as 5, 10, 20, 30, and 50 minutes.

2. Experimental Methods

2.1. Synthesis of Copper Nanoparticles. The schematic diagram of the laser ablation setup is depicted in Figure 1. To prevent the formation of copper oxide, the copper plate (99.99% purity; Sigma Aldrich, St. Louis, MO) was ablated in the presence of nitrogen gas flow [14]. The copper plate was immersed in 20 mL of walnut oil, and the ablation was carried out via a pulsed Q-Switched Nd:YAG laser (Brilliant) at durations of 5 ns, a repetition rate of 10 Hz at wavelength of 1064 nm. To disperse the NPs in the oil, a magnetic stirrer was used during the ablation process. The laser beam was focused on the target with a 300 mm focal length lens for 5, 10, 20, 30, and 50 minutes at room temperature with spot size about 0.7 mm. The characterization tests of UV-visible and Fourier transform infrared spectrum (FT-IR) were conducted using UV-visible double beam photo spectrometer (Shimadzu, Columbia, MD) with a 1 cm optical path cell and FT-IR spectrometer (Spectrum 100, PerkinElmer). The morphology and concentration of the Cu-NPs were determined by transmission electron microscopy (TEM, Hitachi H-7100; Hitachi, Chula Vista, CA) and atomic absorption spectroscopy (AAS, S series), respectively. The refractive indices of walnut oil and the nanofluids were measured using the surface plasmon resonance technique to discriminate variation in the refractive index for the walnut oil in the presence of different concentrations of Cu-NPs.

2.2. Surface Plasmon Resonance Setup. Surface plasmon resonance is acknowledged as the best and most accurate method for measuring the refractive index of nanomaterials. Using this approach allows for propagation of the surface plasmon waves (SPWs) on the interface between a metal layer and a dielectric medium [20]. Essentially, SPWs should be excited with a laser beam in the resonance condition. The resonance condition results from the cross-point of the dispersion curves of the surface plasmon and photon if meeting the requirements of the energy and momentum conservation law [21], as follows:

$$n_p \sin\theta = \sqrt{\frac{n_1^2 n_2^2}{n_1^2 + n_2^2}}. \tag{1}$$

n_p, n_1, and n_2 are the refractive indices for the prism, metal, and dielectric, respectively, and θ is the angle of resonance. In fact, $k_0 n_p \sin\theta$ is the wave number of the photon that is parallel to the interface of the mediums, and $k_0\sqrt{(n_1^2 \times n_2^2)/(n_1^2 + n_2^2)}$ is the wave number of the surface plasmon.

To obtain the resonance angle (θ_R) and the real (n) and imaginary (k) parts of the refractive index of the nanofluid, the SPR signals are analyzed by a minimization of the sum [22]:

$$\Gamma = \sum_{\theta} \left[R_{\text{Exp}}(\theta_2) - R_{\text{Theory}}(\theta_2) \right], \tag{2}$$

where R_{Exp} and R_{Theory} are the experimental and theoretical reflectance, respectively.

The SPR setup is illustrated in Figure 2. The setup consists of a precision rotation stage, a photodiode, He-Ne laser, a polarizer, lock in amplifier, and a high index prism. The rotation stage involved rotating from 45° to 80° and stopping for a moment to register the light intensity and angle. Then, the SPR signal was analyzed using computer software [23].

3. Results and Discussion

The optical absorption spectra for the pure walnut oil and the walnut oil with Cu-NPs are presented in Figure 3. The baseline was calibrated as the reference for the pure walnut oil before the irradiation of the copper plate. As shown in Figure 3, the UV-visible peaks appeared at 615 nm, 606 nm, 588 nm, 576 nm, and 561 nm for the prepared Cu-NPs at 5, 10, 20, 30, and 50 minutes, respectively. These peaks rise

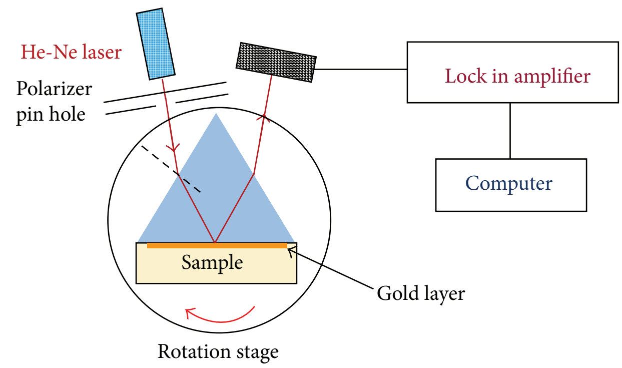

Figure 2: SPR setup to characterize the Cu-NPs samples. The setup consists of a photodiode, a He-Ne laser, a polarizer, a pinhole, a lock in amplifier, a rotation stage, and a high refractive index prism (ZF52).

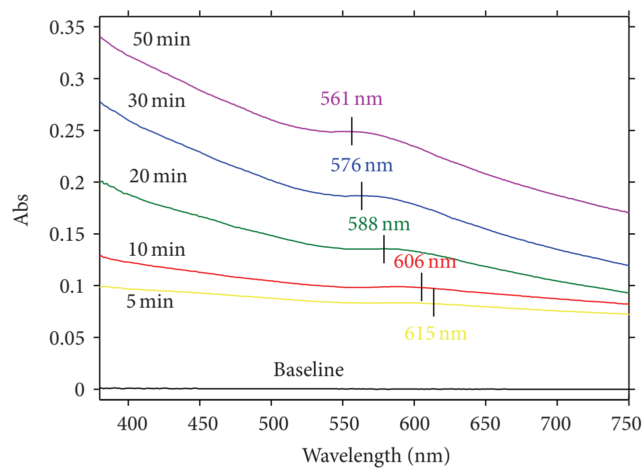

Figure 3: UV-visible spectra of Cu-NPs in walnut oil. The baseline is pure walnut oil, and the UV-visible peaks have blue shift from 615 nm to 561 nm. So, the particle size decreases with increasing the ablation time.

from the localized surface plasmon resonance of the Cu-NPs, which allows for the formation of NPs in walnut oil and authenticates the fact that the NPs are spherical shapes. The peak intensity increased under the influence of increases in the ablation time and concentration of Cu-NPs in walnut oil.

In addition, the concentration of Cu-NPs, measured by atomic absorption spectroscopy (AAS), increased from 2.3 to 112.6 mg/L (see Figure 4(a)); meanwhile, the volume fraction of Cu-NPs was calculated using the following equation [14]:

$$V = \frac{V_p}{V_p + V_L}, \tag{3}$$

where V_L and V_p are the volume of the walnut oil and the volume of the Cu-NPs (m/ρ, where ρ and m are the mass density of the copper and the particles mass dispersed in the walnut oil, resp.). Hence, (4) was derived from a modification and a simplification of (3) as follows:

$$V = \frac{C_{\text{Particle}}}{C_{\text{Particle}} + \rho}, \tag{4}$$

where C_{Particle} are the concentrations of the Cu-NPs obtained from the AAS. Therefore, the volume fraction of nanoparticles increased as the result of an increase in ablation time from 0.0257×10^{-5} to 1.26×10^{-5}. The pure walnut oil and nanofluid parameter values are presented in Table 1.

Figure 5 is the TEM pattern of Cu-NPs in walnut oil. It depicts the morphology of Cu-NPs dispersed in walnut oil which take on a spherical shape. The UTHSCSA image tool (version 3, UT Health Science Center) was used to analyze the captured images to determine the particle size. As a result, the particle size decreased from 25 nm to 4.01 nm while the ablation time and distribution of the particles increased.

At first, the Cu-NPs formed through phase transition and nucleation; hence, crystals of the Cu cluster expanded from released copper atoms, and the fatty acid chain of walnut oil capped the Cu-NPs. Afterward, the laser beam interacted with the target and the nanoparticles which were released in nanofluid and the Cu-NPs were ablated and broken to a small size (Figure 5(c)). Therefore, the particle diameter decreased as the ablation time increased (Figure 4(b)) [24].

The FT-IR spectrum analysis of nanofluids is illustrated in Figures 6(a) and 6(b). The spectra were registered at

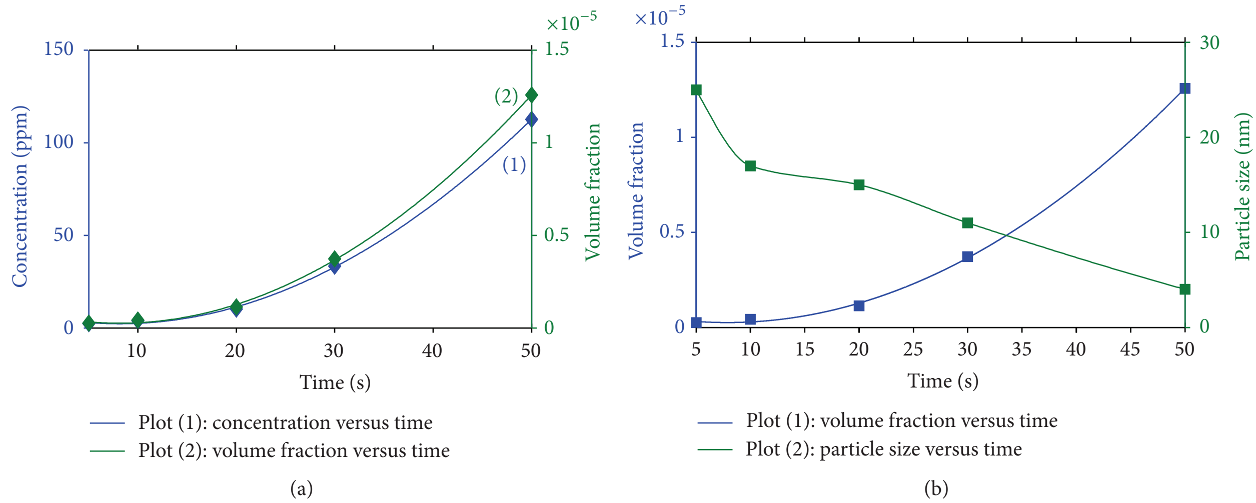

Figure 4: (a) Variation of nanoparticles concentration and volume fraction with ablation time. (b) Variation of volume fraction and nanoparticles size with ablation time.

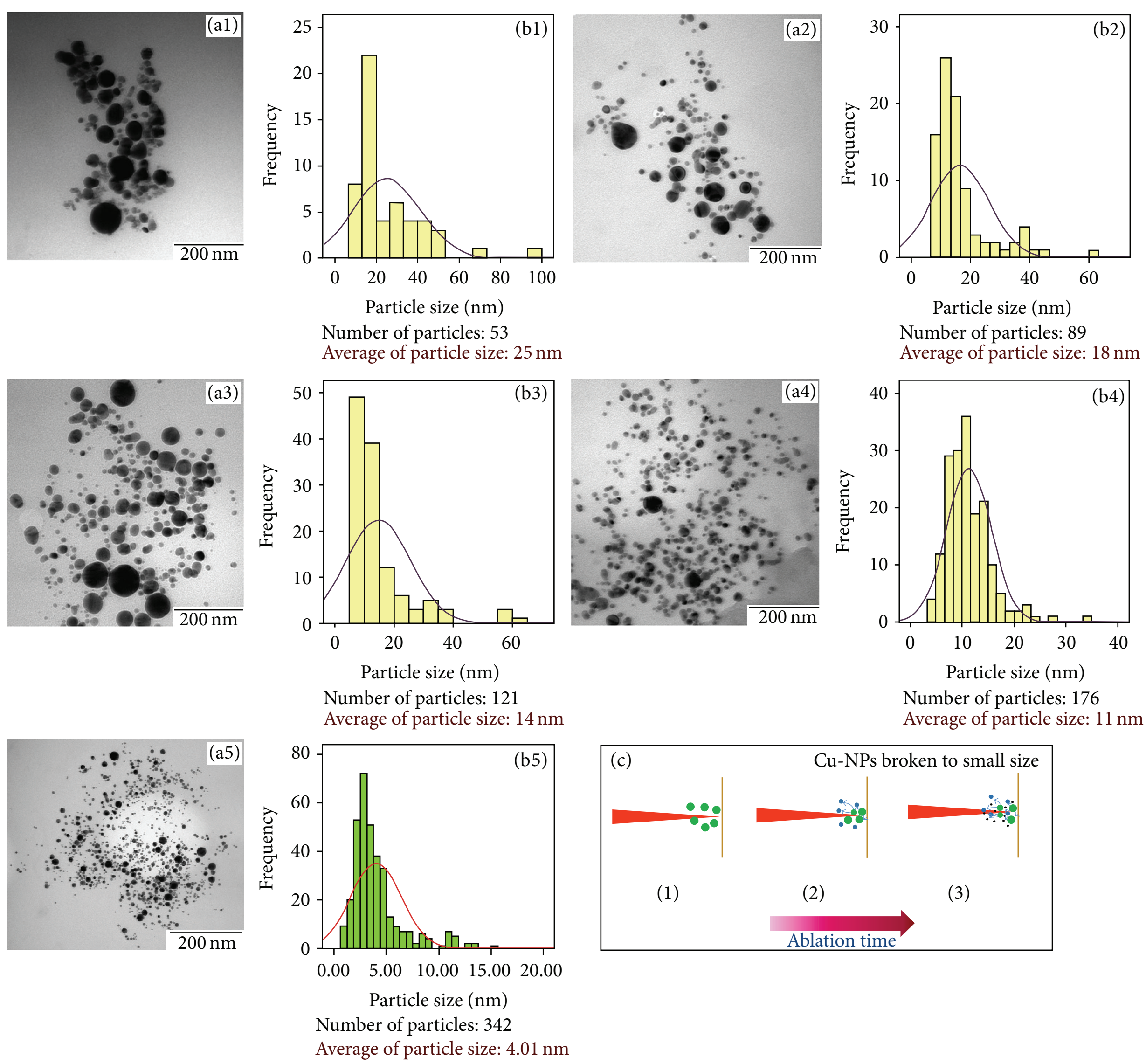

Figure 5: TEM images show the morphology, distribution, and particle size of Cu-NPs in walnut oil with different ablation time. The Gaussian curves were fitted to the size bar chart and the particle size was in the range of 25 nm to 4.01 nm.

TABLE 1: The pertinent parameters of pure walnut oil and copper nanofluid.

Sample	Concentration of Cu-NPs (ppm)	Volume fraction ($\times 10^{-5}$)	Average particle size (nm)	Real part of refractive index (n)	Imaginary part of refractive index (k)	Resonance angle (θ_R)	Reflectance
Pure walnut oil	—	—	—	1.4691	0.002	62.819°	0.0362
5 min	2.3	0.0257	25	1.4691	0.008	62.854°	0.0905
10 min	3.8	0.0424	17	1.4690	0.012	62.874°	0.1278
20 min	10.2	0.1138	15	1.4688	0.026	62.966°	0.2437
30 min	33.4	0.3728	11	1.4686	0.032	62.995°	0.2846
50 min	112.6	1.26	4.01	1.4682	0.043	63.042°	0.3455

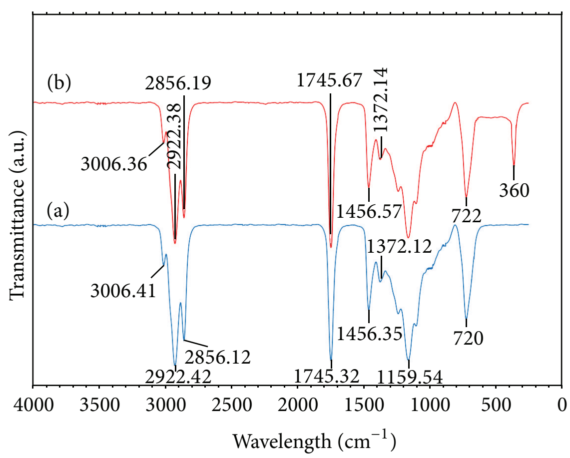

FIGURE 6: FT-IR results: (a) pure walnut oil, (b) walnut oil with Cu-NPs (nanofluid).

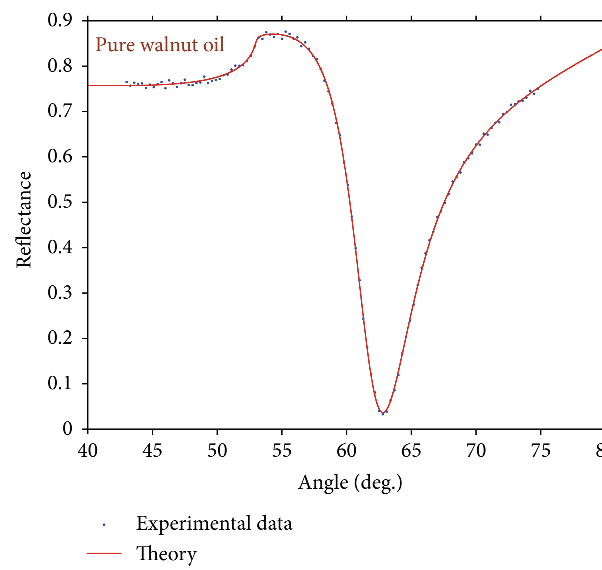

FIGURE 7: SPR signal related to pure walnut oil. The resonance angle is 62.819° which corresponds to 1.4691 + 0.002i refractive index.

a wavelength ranging from 250 cm^{-1} to 4000 cm^{-1}. The FT-IR spectra are shown as a chemical structure before and after ablating the copper plate. Figure 6(a) shows the FT-IR spectrum of the pure walnut oil where the peaks at 3006.41, 2922.42, 2856.12, and 1745.32 cm^{-1} related to the =C-H stretching vibration, CH_2 asymmetric, symmetric, and -C=C stretching ester carbonyl function group of triglycerides, respectively.

In addition, the peaks of 1456.35, 1372.12, 1159.54, and 720 cm^{-1} corresponded to the CH_2 bending, -C-O stretching vibration, and -CH_2 bending (*cis* -CH=CH- bending). The FT-IR spectrum after ablation of the copper plate is demonstrated in Figure 6(b). In the synthesis of Cu-NPs in walnut oil, the peaks at 3006.39, 2922.38, 1745.67, 1456.57, 1372.14, 1158.87, and 722.01 cm^{-1} confirm the stability of the molecular structure and functional groups. Also, the peaks appearing in 360 cm^{-1} are related to Cu-NPs [25]. The tail of the carbonyl band capped the Cu-NPs through the electron transfer from the carboxylic group to Cu-NPs; as a result, the motion of molecules was impeded inside the particular area and the entropy decreased [26, 27]. This proves that a long hydrocarbon chain prevents the agglomeration of Cu-NPs.

The SPR technique is a versatile method for measuring the real and imaginary parts of a nanofluid as it relies on the refractive index of the medium and the concentration of Cu-NPs in the walnut oil. Figure 7 shows the SPR signal for pure walnut oil where the resonance angle occurred at 62.819°, which is equivalent to the 1.4691 + 0.002i refractive index.

Figure 8 shows the relationship of the SPR and optical properties of the copper nanofluid. The resonance angle shifted from 62.854° to 63.042° and the reflectance increased as a result of an increase in the volume fraction of Cu-NPs. This is due to the increase in absorption and imaginary parts of the refractive index of the nanofluid.

Figures 9(a) and 9(b) show the variation of real and imaginary parts of refractive index of nanofluid. Consistent with the Kramers-Kroning relationship, the real part of the refractive index decreased as a consequence of an increase in the imaginary part [28]. The volume fraction of Cu-NPs changed from 0.0257×10^{-5} to 1.26×10^{-5}, so the scattering cross section of nanofluid increased (Figure 4(b)); therefore, the absorption and the imaginary part of nanofluid heightened. The experimental results are summarized in Table 1.

4. Conclusion

The Cu-NPs were dispersed in walnut oil using laser ablation. The UV-visible peaks appeared at 615 nm, 606 nm, 588 nm,

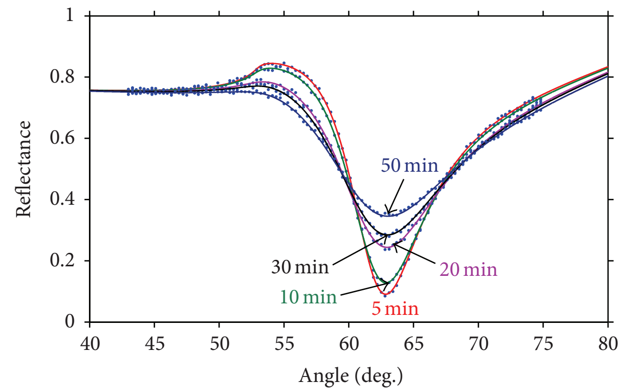

Figure 8: SPR signals for measurement of the refractive index of the nanofluid in different ablation time.

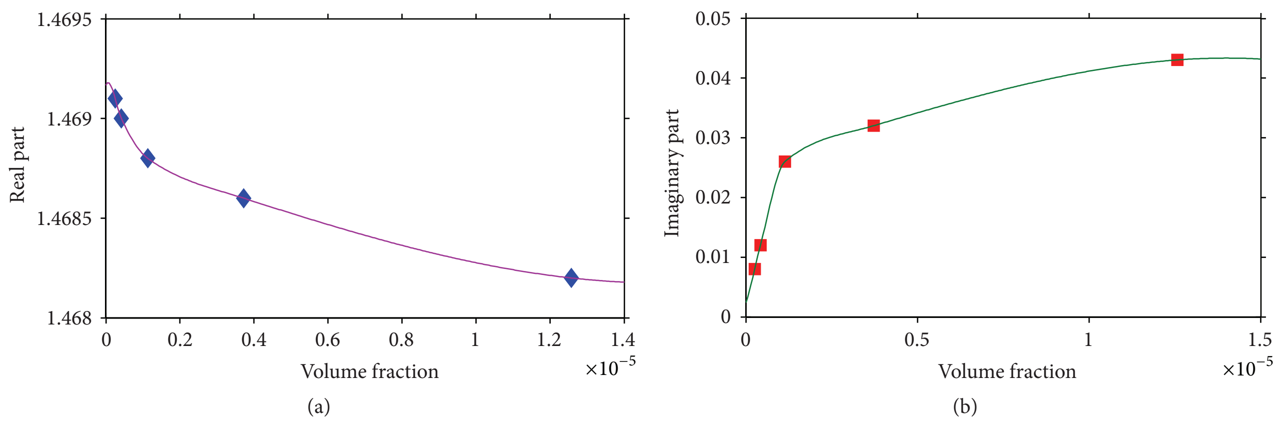

Figure 9: (a) The real part of refractive index decreased by increasing the volume fraction of nanofluid. (b) The imaginary part of refractive index increased by increasing the volume fraction of nanofluid.

576 nm, and 561 nm, and particle size decreased from 25 nm to 4.01 nm in a spherical shape with an increase in the concentration of Cu-NPs from 2.3 to 112.6 ppm. As in FT-IR results, the tail of the carbonyl band capped the Cu-NPs through the electron transfer from the carboxylic group to Cu-NPs. The refractive index was obtained using the SPR technique and shifted from 1.4691 + 0.008i to 1.4682 + 0.043i. The synthesis of Cu-NPs did not require any agent or extra chemical component. Based on these characteristics, the laser ablation contributes as a green and suitable method to the preparation of Cu-NPs in walnut oil. Therefore, the preparation of Cu-NPs in walnut oil is suggested for future activity to prepare the skin cream or skin lotion, and the effect of particle size and concentration of particles in walnut oil are the objective in future research.

Competing Interests

The authors declare that they have no competing interests.

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