International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2024: 7.101

Second Harmonic Generation Efficiency of Copper Nanoparticles Synthesized via Pulsed Laser Ablation in Liquid (PLAL)

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Abstract: ***This study investigates the second harmonic generation (SHG) efficiency of copper nanoparticles synthesized through pulsed laser ablation in liquid (PLAL) using a 1064 nm Nd:YAG laser. The nanoparticles, formed in deionized water, exhibited an average size of 32–45 nm and were characterized via SEM and UV-Vis spectroscopy, revealing a plasmonic resonance peak at 574 nm. The nonlinear optical response was assessed by rotating the nanoparticle solution and measuring SHG intensity at varying angles and laser powers (50 and 85 mW). The results demonstrated peak SHG efficiency at a 5° incident angle, highlighting the potential of copper nanoparticles for applications in nonlinear optics and photonic device design.***

Keywords: Cu Nanoparticles, Second Harmonic Generation, efficiency, Pulse Laser Ablation in Liquid, nanophotonics

1. Introduction

Self-energy generation in Cu particles arises due to surface plasmon effects, especially in centrosymmetric materials [1]. This coupling of localized surface plasmon resonances enhances self-energy generation by several orders of magnitude, even to higher-order harmonics [2]. This effect enhances the applicability of copper nanoparticles in nonlinear nanophotonic systems [3]. Advances in material stability and hybrid plasmonic structures have enabled robust and enhanced self-energy generation [4]. As long as the size of Cu nanoparticles remains smaller than the wavelength of light, the generation of second harmonics will be a second-order nonlinear optical property [5]. This technique regulates the efficient conversion of invisible (infrared) light to visible light [6], a characteristic of this material, in addition to its catalytic, thermal, and electrical properties [7]. The ability of hybrid copper-gold nanoparticles and oxides to generate harmonics was investigated [8]. Second harmonic generation is a second-order nonlinear optical process in which two photons of the same frequency ω are combined to generate a photon with a doubled frequency 2ω [9]. The conversion efficiency represents the ratio of the resulting harmonic radiation intensity $I_{2\omega}$ to the incident fundamental radiation intensity I_{ω}, as shown in the following formula [10].

$$\eta_{SHG} = \frac{I_{2\omega}}{I_{\omega}} \ldots\ldots\ldots\ldots\ldots (1)$$

Several factors affect the conversion efficiency, including the properties of the nonlinear medium, such as the shape and size of the particles [11], the type of medium surrounding the particles [12], the wavelength of the laser used [13], and the laser pulse duration [14]. The novelty of this research lies in the use of PLAL synthesis technique to prepare Cu particles from pure elemental materials, characterize these particles, and determine their size and shape. A few researchers focused on their ability to generate harmonics. Therefore, this research focuses on generating second harmonics from a pulse laser with a wavelength of 1064 nm, an energy of 1.5 joules, and a pulse duration of 1 nanosecond. This study aims to evaluate the second harmonic generation efficiency of copper nanoparticles synthesized via pulsed laser ablation in liquid using a 1064 nm Nd:YAG laser.

2. Experimental Section

2.1 Materials

A piece of high purity copper (99.9%) (atomic number 29, atomic weight 63.546 atomic mass units), deionized water, and a laser with a wavelength of 1064 nm, power of 1.5 J, and a repetition rate of 6 Hz were used to prepare the nanoparticles. For SHG A beam splitter, 1064 nm laser with power (85 and 50) mW, optical filters to isolate the signal at double frequency, and a sensitive detector connected to a lock-in amplifier to accurately measure the intensity were used.

2.2 Methods

The copper sample was placed at the bottom of a glass beaker containing 5 ml of deionized water. A 1064 nm Nd: YAG laser beam with power of 1.5J was directed perpendicularly (90°). The target was ablated for 15 minutes and the liquid turned green, indicating successful nanoparticle formation (see Fig. 1a). The nanoparticle solution was placed in a quartz cell and placed on a rotating table with angles ranging from 30 to -30°. The sample was moved angle by angle and the intensity of the transmitted laser radiation was measured using a detector as shown in Fig. 1b.

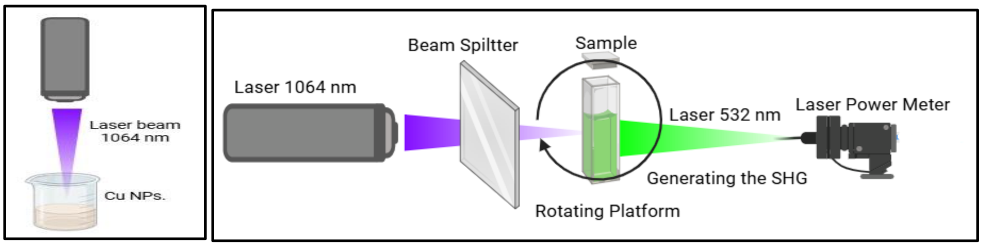

Figure 1: Experimental setup a. PLAL technique, b. SHG by 1064 nm

3. Results and Discussion

This investigation addresses a gap in current research by demonstrating efficient SHG from physically synthesized copper nanoparticles, offering potential for integration into next-generation photonic devices.

3.1 Characterization of Cu nanoparticles

Using UV-Visible spectroscopy, an absorbance versus wavelength curve was obtained for copper nanoparticles prepared by pulsed laser ablation in liquid. The surface plasmon resonance peak was observed at 574 nm, indicating the formation of copper nanoparticles as shown in Figure 2a. While the average crystallite size of the particles was calculated using the sheerer equation by finding the Full width at a half maximum Table 1. Data analysis reveals peaks at 39.5° and 41.6°, corresponding to the highest intensity as shown in Figure 2b.

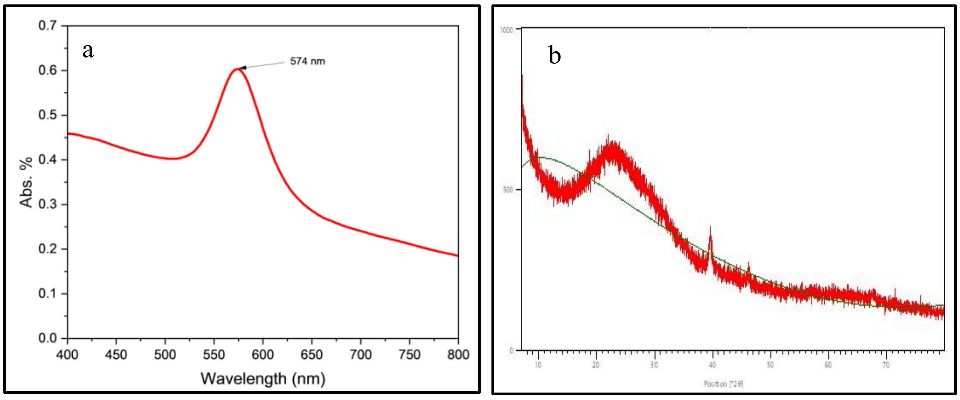

Figure 2: The Characterization of the synthesis Cu a. the absorbance curve. b. the XRD analysis

Table 1: The FWHM and d-spacing at 2θ

[°2θ]	FWHM [°]	d-spacing [Å]
39.5800	0.5331	2.27513
46.1767	0.0220	1.96430

3.2 The analysis of scanning electron microscopy

As shown in Figure 3 the spherical shape of the particles was confirmed using scanning electron microscopy, indicating an average particle size of 32 nm.

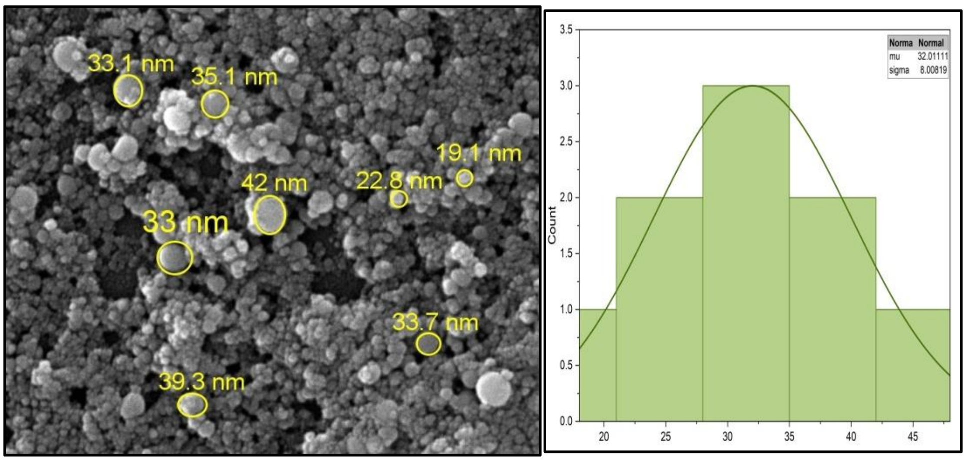

Figure 3: The SEM with spherical nanoparticles and the distribution of the particles size

3.3 Efficiency of Second Harmonic Generation for Cu NPs.

The conversion efficiency of copper nanoparticles was calculated using Eq. 1. It is observed that the intensity of the second harmonics changes as the sample is rotated. This reveals the surface symmetry of the nanoparticles. According to the Eq 1. the intensity changes as the generated signal is indeed second-order harmonics, as $I_{2\omega}$ is linearly proportional to the incident fundamental radiation

Paper ID: SR251114005911 DOI: https://dx.doi.org/10.21275/SR251114005911

intensity I_ω. Figure 4 shows the second harmonic intensity curve at different rotation angles and with two laser powers: 85 and 50 mW. The highest observed intensity was 94% at a 5° incident angle.

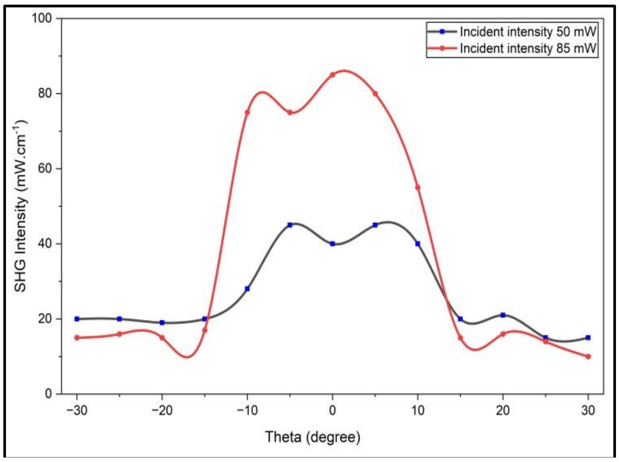

Figure 4: The Intensity of SHG at 50 and 85 mW.

Table 2: The SHG efficiency of Cu NPs.

Incident angle (deg.)	SHG efficiency (at 50mW) %	SHG efficiency (at 85mW) %
30	40	11.76471
25	40	16.47059
20	52	18.82353
15	50	17.64706
10	88	64.70588
5	100	94.11765
0	90	100
-5	100	103.5294
-10	66	88.23529
-15	50	20
-20	48	17.64706
-25	50	18.82353
-30	50	17.64706

4. Conclusion

The synthesis of spherical copper nanoparticles via pulsed laser ablation in liquid resulted in particles with a mean size of 32 nm and a surface plasmon resonance at 574 nm. The nonlinear optical analysis demonstrated peak SHG efficiency at a 5° incident angle, confirming the nanoparticles' suitability for nonlinear photonic applications. These findings support the potential use of physically synthesized copper nanoparticles in the development of an advanced photonic device. Future research should explore optimization of particle shape and medium interactions to further enhance SHG response.

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