LASER APPLICATION TO PRODUCE COPPER NANOPARTICLES IN SOME DIFFERENT LIQUIDS

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Abstract. Copper nanoparticles are difficult to produce since they oxidate or aggregate easily. We studied to use Nd:YAG laser to produce copper nanoparticles in clean liquids such as distilled water, deionized water , ethanol and acetone. The role of laser fluence, laser irradiation time were determined for optimal laser ablation process. The TEM and spectral measurements were carried out to determine average size and size distribution of copper nanoparticles. There was no indication of the absorption peak around 800 nm which is typical of copper oxide nanoparticles except the characteristic peak around 600 nm of the copper nanoparticles in absorption spectra. The experimental results showed advantages of the laser ablation method.

Keywords: Surfactant, Plasmon resonance, laser ablation.

I. INTRODUCTION

In recent years, cooper nanoparticles have attracted great interest because of their potential applications in conductive films, nanofluids and catalysis [1]. Furthermore, copper nanoparticles embedded in a dielectric medium such as polymer matrices are potential materials for nonlinear optical devices [2]. Number of methods including microemulsion, reverse micells and reduction of copper salts have been developed to produce copper nanoparticles. Recently, pulsed laser ablation was employed for preparation of metal and semiconductor materials in different media such as vacuum, reactive gas and liquid. Pulsed laser ablation in liquids provides a simple, flexible method to prepare metal and semiconductor nanoparticles. One of the advantages of the laser ablation in comparison with other conventional methods is the synthesis of nanoparticles in clean liquid environment with ease and without contamination by a reducing agent. This method makes possible the production of pure nanoparticles in biologically-friendly environment.

Although several metal nanoparticles such as gold and silver nanoparticles have been prepareed so far, copper nanoparticles are difficult to produce since they oxidate or aggregate easily. We studied to prepare copper nanoparticles by pulsed laser ablation in some clean liquids and aqueous solutions.

II. EXPERIMENTS

The schematic diagram of the experimental setup used in this experiment is shown in Fig. 1. The laser source used for ablation in the experiments was a Nd: YAG laser (Quanta Ray Pro 230 Newport USA) in Q-switching mode which gives laser pulses with energy of up to 1200mJ, pulse duration of 8 nanoseconds and repetition rate of 10Hz.

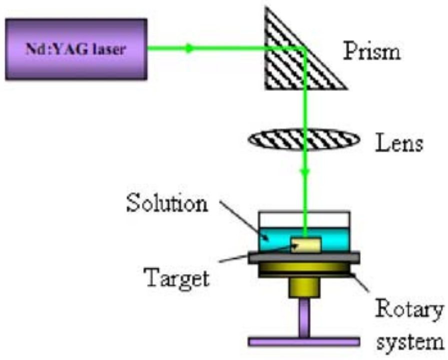


Fig. 1. *Experimental setup.*

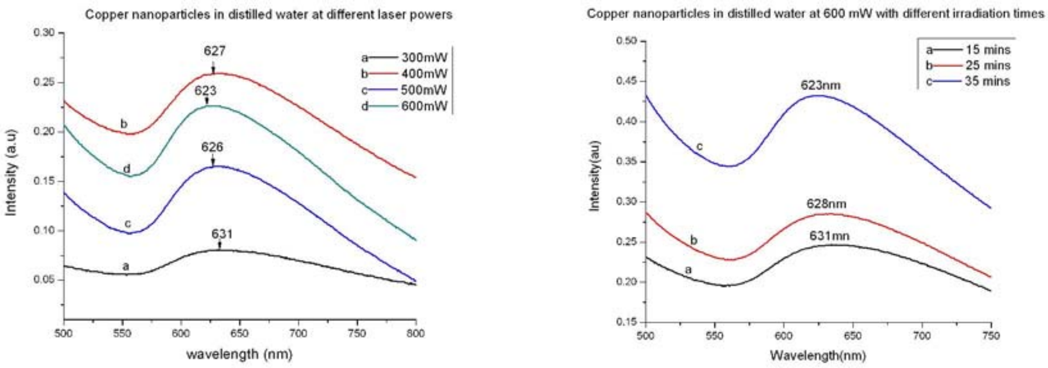
We used the fundamental wavelength (1064 nm) of the Nd: YAG laser to ablate a copper plate (99,9% used in purity) which was placed in a glass cuvette filed with 10ml aqueous solution of surfactant . The laser beam was focused on the copper plate by a lens having the focal length of 150mm. Several different liquids including distlled water, solution of PVP in distilled water, deionized water, ethatnol and acetone were used as surfactant. The vessel was placed on a horizontal platform, which executed repetitive circular motions at a constant speed to prevent agglomeration of particles. The copper nanoparticle colloid was extracted for absorption measurement and TEM observation. The absorption spectrum was measured by a Shimadzu UV-2450 spectrometer. The TEM micrograph was taken by a JEM 1010-JEOL. The size of nanoparticles was determined by ImagieJ 1.37v software of Wayne Rasband (National institutes of Health, USA). The size distribution was obtained by measuring the diameter of more than 500 particles and using Origin 7.5 software. The copper nanoparticles were produced with different laser powers and irradiation time. The average size and size distribution of copper nanoparticles were observed to determine the optimal laser ablation process.

III. RESULTS AND DISCUSSION

In laser ablation method the nucleation, growth, and aggregation mechanisms depend on several factors including laser wavelength, pulse energy, pulse duration, repetition rate and nature of liquid environments [3]. First, we studied the regime of laser fluence and laser irradiation time in pulsed laser ablation process to determine suitable ablation procedure. Then, we studied the effect of different liquids environment in average size and size distribution of copper nanoparticles.

III.1. Preparation of copper nanoparticles in distilled water

Keeping the irradiation time of 15 minutes we ablated a copper plate in distilled water by 1064nm wavelength of Nd:YAG laser with different average power (300, 400, 500 and 600mW respectively) . The absorption spectra of the prepared copper nanoparticle colloids were presented in Fig .2(a). We observed the characteristic Plasmon resonance peak around 620 nm of the copper nanoparticles in the absorption spectra. There was no indication of the absorption peak around 800 nm which is typical of copper oxide nanoparticles. When the average laser power increases from 300mW to 600mW the Plasmon resonance peak shifts to the shorter wavelengths. Taking the average laser power of 600mW we ablated the copper plate with different irradiation times. Fig 2(b) shows the absorption spectra of cooper nanoparticles prepared in distilled water with irradiation times from 15 to 35 minutes. TEM image and corresponding size distribution of copper nanoparticles prepared in distilled water by average laser power of 600mW and laser irradiation time of 15 minutes were presented in Fig.3.



(a) **(b)**

Fig. 2.*The absorption spectra of Cu nanoparticle colloids prepared in distilled water by different average laser power (a) and laser irradiation time (b)*

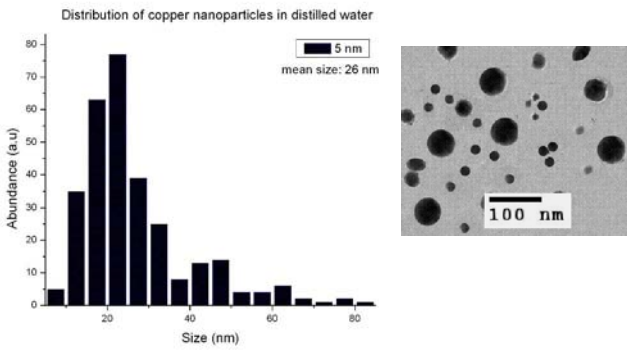
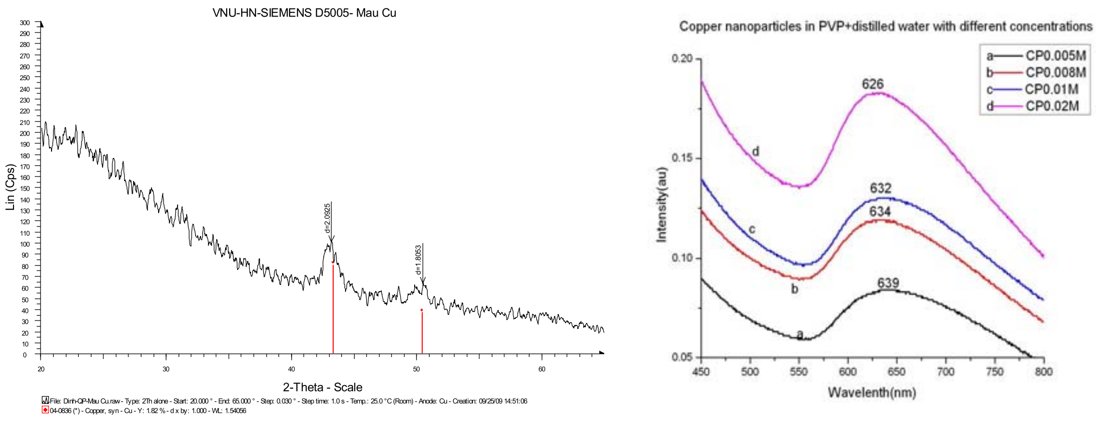


Fig. 3. *TEM image and corresponding size distribution of the copper nanoparticles prepared in distilled water by average laser power of 600mW and irradiation time of 15 minutes*

As seen in TEM image, the copper nanoparticles are rather spherical in shape. Analysis from size distribution shows the mean diameter of copper nanoparticles is 26nm in distilled water. The copper nanoparticles colloids prepared in water remained stable for a week.

XRD pattern of the Cu nanoparticles was also observed in powder form. The result is shown in Fig.4(a). There are peaks at 2θ = 43,39 and 50,47 degree corresponding to planes (111) and (200) respectively



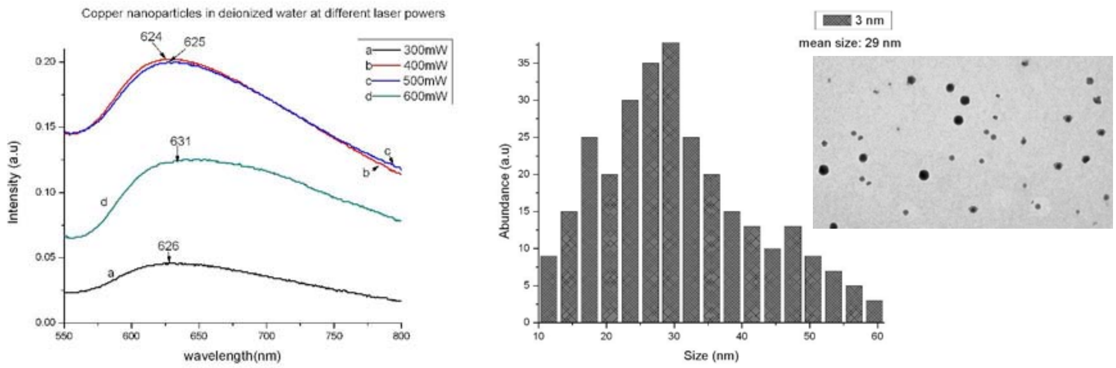
(a) **(b)**

Fig. 4.*The XRD pattern of copper nanoparticles (a) and the absorption spectra of copper nanparticle colloids prepared in solutions of PVP with different concentration (b)*

In order to remain copper nanoparticles more stable we ablated copper plate in solution of Polyvinyl pyrrolidone $(C_6H_9NO)_n$-PVP in distilled water with different concentrations. In the presence of PVP, the oxygen atoms of C=O group are attached to the Cu atoms on the nanoparticle surface [5]. The PVP protected Cu nanoparticles remained stable more than 2 weeks. In addition, our results show the Plasmon resonance peak was shifted to shorter wavelength in the absorption spectra when the concentration of PVP increases from 0.005M to 0.02M (Fig.4(b)). That means average size of copper nanoparticles decreases respectively.

III.2. Preparation of copper nanoparticles in deionized water, ethanol and acetone

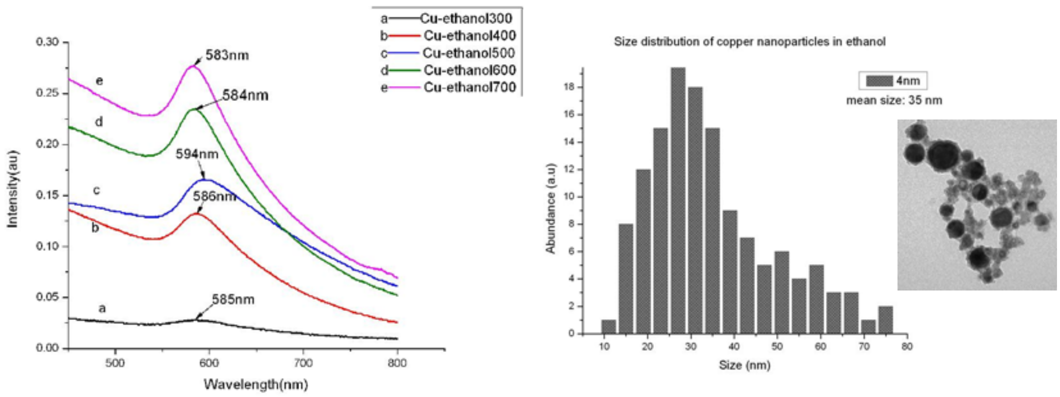
Using the same method we studied to prepare copper nanoparticles in some different clean liquids including deionized water, ethanol and acetone. The results were presented in Fig 5, 6, 7 respectively.



(a) **(b)**

Fig. 5. *The absorption spectra of Cu nanoparticles prepared in deionized water by different average laser power (a) and TEM image and size distribution of Cu nanparticles prepared by average laser power of 500mW, laser irradiation time of 15 minutes.(b) .*

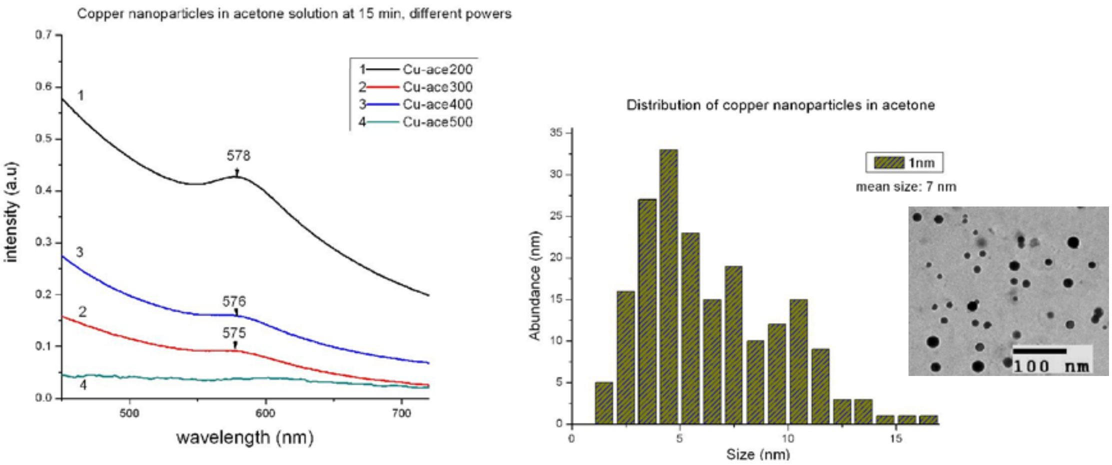
The copper nanoparticles prepared in deionized water by average laser power of 500mW with irradiation time of 15 minutes had mean diameter of 29nm and remained stable for 5 days .



(a) ***(b)***

Fig. 6. *The absorption spectra of Cu nanoparticles prepared in ethanol by different average laser power (a) and TEM image and size distribution of Cu nanparticles prepared by average laser power of 500mW, laser irradiation time of 15 minute (b).*

The copper nanoparticles prepared in ethanol by average laser power of 500mW with irradiation time of 15 minutes had mean diameter of 35nm and remained stable for 2 weeks.



(a) ***(b)***

Fig. 7. *The absorption spectra of Cu nanoparticles prepared in acetone by different average laser power (a) and TEM image and size distribution of Cu nanparticles prepared by average laser power of 200mW, laser irradiation time of 15 minutes (b).*

The copper nanoparticles prepared in acetone by average laser power of 200mW with irradiation time of 15 minutes had mean diameter of 7 nm and remained stable about 3 weeks.

We can see in the Fig 5(a), 6(a) and 7(a) the complicated effect of average laser power or laser fluence on the formation of copper nanoparticles in different liquids. The mechanism of pulsed laser ablation of metal in liquids could be explained by a model of Mafune and his coworkers[6]. At first, pulsed laser beam ablates the target during laser irradiation. Ablated materials, which are called plume, expand under liquid environment and disperse many produced species. Dispersed materials include nanopartilces, small clusters, free atoms and ions. For the first few pulses, only liquid medium surrounds the plume and metal species in plume nucleate to produce nanoparticles. The nanoparticles disperse in liquid medium and provide nucleation centers for the next incoming metal species. Plume-nanoparticle interaction takes place. In this stage, two mechanisms contribute to the nucleation process. The first mechanism is direct nucleation of metal in the condense plume similar to the first stage. Another mechanism is addition of the metal species to the nanoparticles that produced before. When both mechanisms occur, broad size distributions will be observed. The laser fluence takes a very important role in formation and growth mechanism of nanoparticles. We need to determine laser fluence regime for suitable ablation procedure in each used liquids.

IV. CONCLUSION

Using Nd:YAG nanosecond laser we studied and prepared successfully copper nanoparticles by laser ablation method in different clean liquid environments. The regime of average laser power and laser irradiation time were determined for each laser ablation procedure. The experimental results showed advantages of the laser ablation method to prepare pure copper nanoparticles.

V. ACKNOWLEDGMENTS

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