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Comparative study on Cu, Al and Cu-Al alloy nanoparticles synthesized through underwater laser ablation technique

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Abstract: In this work, we have done a comparative study on Cu, Al and Cu-Al alloy nanoparticles synthesized through underwater pulsed laser ablation technique. Second harmonic of Nd: YAG nanosecond pulsed laser with 50 J/cm² fluence was used to ablate the Cu (99.99%), Al (99.99%) and Cu-45% Al alloy targets. However, the laser synthesis of Cu-Al alloy nanoparticles is not yet investigated best of our knowledge. Thus, it is the first time we have synthesized alloy nanoparticles through underwater laser ablation in a chemical free environment. Moreover, we have used abundant earth metals to synthesize the nanoparticles. The particles morphology, shape and size were analysed through SEM and DLS analysis where we have observed that the average size of alloy nanoparticle was much smaller than its monometallic counterparts. The crystallinity and elemental analysis of synthesized nanoparticles were studied through XRD and EDS respectively. The alloy formation of nanoparticles was evident from such structural investigations. Further a comparative study on optical properties of alloy and monometallic particles were investigated through UV-Vis absorption spectroscopy. Alloy particle shows a remarkable improvement in optical absorption in comparison to its parent materials.

1. Introduction:

Laser ablation in liquid environment is a promising top-down approach to generate nanoparticles[1]. This is a favorable technique where laser energy is used to synthesize the particles in chemical free environment from variety of materials [2]. Laser parameters like laser wavelength, laser fluence and pulse duration have significant effect towards the particle shape, size and concentration of colloidal solution [3]. Number of studies have been done on noble metals like Au and Ag, synthesized through underwater ablation technique. However, the availability and cost effectiveness should be addressed while analyzing with noble metals. Hence, the copper and aluminum nanoparticles have attracted great attention due to their low cost, high conductivity and easy availability compared to the noble metals [4, 5]. Such metal nanoparticles are mostly used for optical, electronic and catalytic applications due to their unique properties. Moreover such nanoparticles show good surface Plasmonic property in UV and visible range of spectrum [6, 7]. Number of literatures are there on Cu and Al nanoparticles synthesized through laser ablation technique. Miranda et al. have generated copper nanoparticles through laser ablation in liquid and investigated the surface enhance Raman scattering of nanoparticles [8]. Whereas, Kumar et al. have investigated the pulsed laser synthesis of copper nanoparticles in ambient air and water [9]. There are reports on optical properties of Cu nanoparticles where Cu NPs are synthesized through laser ablation in different synthesis medium [10, 11]. Moreover, Oguchi et al. have done little different investigation on underwater laser ablation of Cu where they have studied the effect of pulse duration on plasma plume formation [12]. Besides that, number of studies are there on Al nanoparticles where Shaheen et al. have shown the effect of spot size on formation of Al alloy nanoparticles through laser ablation in air [13]. Hu et al. have done a relative study on femtosecond laser ablation of aluminium in ambient air and water [14]. Furthermore, Dudoitis et al. have done a comparative study on aluminium nanoparticles in different ablation environment (in ambient air and



argon gas) [15]. However the studies on optical absorption of Cu and Al nanoparticles are very limited. It was reported that the extinction spectra of both of the metal particles mostly lie in between UV-Vis range of spectrum [16]. But, the literatures on synthesis of Cu-Al alloy nanoparticles are rarely being discussed [17]. Moreover the optical properties of such bimetallic nanoparticles have not yet been discussed before.

Here, we have synthesized Cu, Al and CuAl alloy nanoparticles with the help of underwater pulsed laser ablation technique where second harmonic (532 nm) of pulsed laser at 50 J/cm^2 fluence were used to generate the nanoparticles. We have done a comparative study towards the size and optical properties of nanoparticles synthesized from different metal targets. It was observed that the size of bimetallic (Cu-Al) particles are comparatively smaller ($\sim 90 \text{ nm}$) than the monometallic one. Moreover, we have noticed that the Cu-Al alloy nanoparticles show improved optical absorption than its monometallic counterparts. Thus, we can claim that we have used abundant earth metals (Cu and Al) to generate nanoparticles and show improved optical absorption.

2. Experimental Setup:

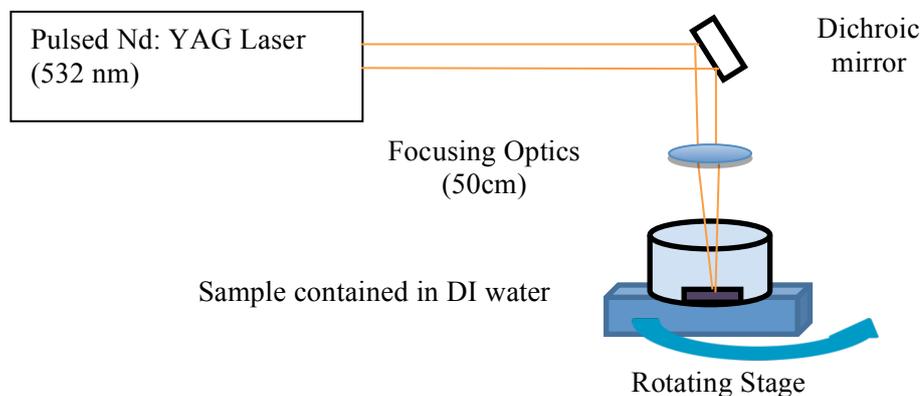


Figure 1. Experimental setup of nanoparticle generation

Figure 1 shows the schematic diagram of underwater nanoparticle generation. Pulsed nanosecond Nd:YAG laser at 532 nm wavelength with 50 J/cm^2 fluence were used to synthesize Cu-Al alloy, Cu and Al nanoparticles from three different metal targets. The pulse duration of laser pulse was 9 ns with 10 Hz of repetition rate. The laser beam was diverted with the help of dichroic mirror and focused on the target (Diameter: 30 mm, thickness: 0.5 mm) surface with a converging lens (focal point: 50 cm). The target materials (Cu-Al, Cu and Al) were placed inside a glass container filled with 20 ml of deionized water which corresponds to the liquid height of $\sim 8 \text{ mm}$ above the target. The glass container along with the target material were rotated in a clockwise direction with a constant speed of 10 RPM by a motorized rotating stage. The ablation time was set to 45 mins for individual laser irradiation. Generated samples were characterized through SEM, EDS, DLS, XRD and Uv-Vis spectrum analysis. The surface morphology and shape of particles were characterized by SEM images whereas the size distribution was studied through DLS analysis. The elemental analysis and crystalline formation were investigated through EDS and XRD respectively. The absorption spectrum of monometallic and bimetallic nanoparticles were detected from UV-Vis spectrum analysis.

3. Results and discussions:

3.1 Investigations on Cu-Al alloy nanoparticles synthesized at 532 nm laser wavelength with 50 J/cm^2 laser fluence:

Figure 2 shows the underwater laser ablated Cu-Al alloy nanoparticles at 532 nm laser wavelength with 50 J/cm^2 laser fluence. The surface morphology of such alloy nanoparticles were observed from SEM image where spherical alloy nanoparticles with average diameter $\sim 90 \text{ nm}$ was detected. The particle size distribution range from 55-145 nm was analyzed from DLS characterization. The crystallinity was examined through XRD analysis whereas the main elements were observed in EDS characterization. The XRD shows the different phases of Cu-Al alloy nanoparticles with their oxidation behavior. The oxidation of nanoparticles is visible from such structural analysis due to the high oxidation potential of Cu and Al. Further, the EDS analysis shows the presence of main elements like Cu, Al, O in the samples. Thus, EDS analysis validates the XRD results which confirms the alloy formation of Cu-Al alloy nanoparticles.

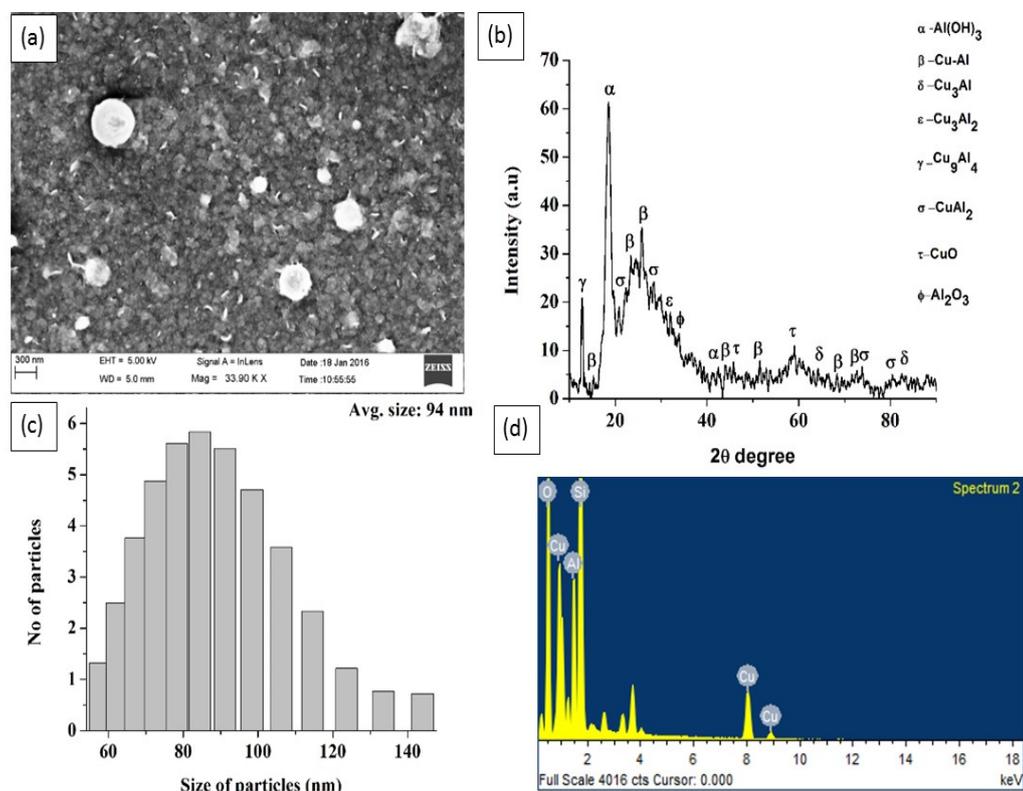


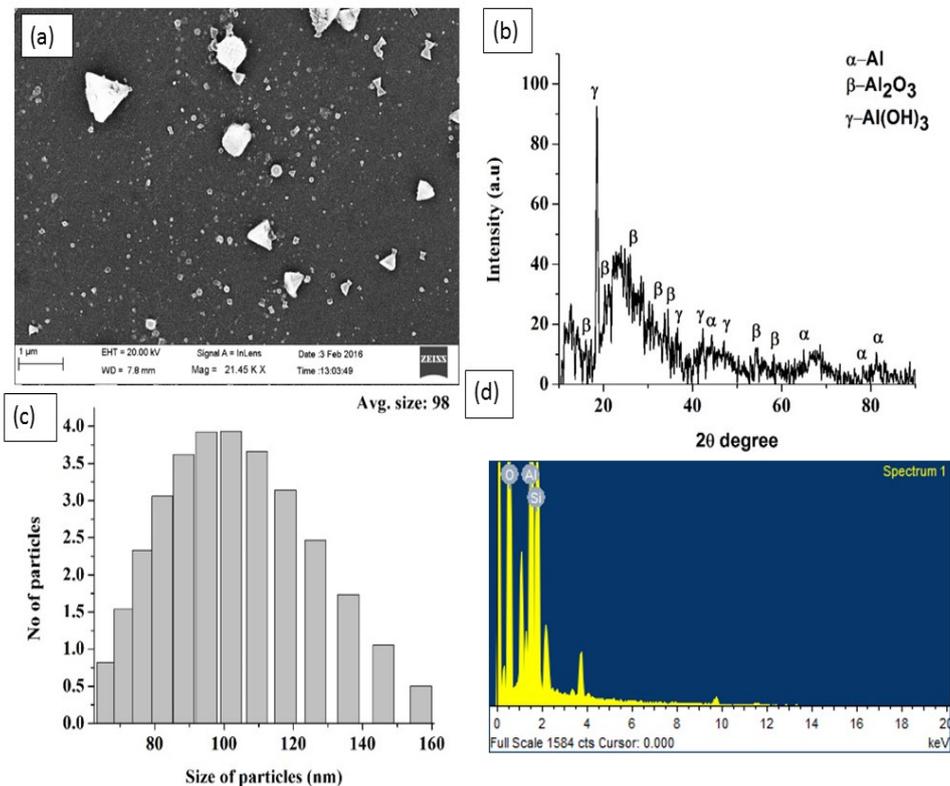
Figure 2. SEM (a), XRD (b), DLS (c), and EDS (d) analysis of laser ablated CuAl nanoparticles

3.2 Investigations on Al nanoparticles synthesized at 532 nm laser wavelength with 50 J/cm^2 laser fluence:

Figure 3 shows the underwater laser ablation of Al nanoparticles synthesized at 532 nm laser wavelength with 50 J/cm^2 fluence. SEM image (figure 3a) has shown the size, shape and surface morphologies of as synthesized Al nanoparticles where particles were detected in spherical shape. Further, particle size distribution was investigated through DLS analysis where average particle size of 98 nm was observed. XRD and EDS characterization shows the crystalline nature of Al nanoparticles. Clear oxide formation due to high oxidation potential of Al nanoparticles was evident from XRD image.

Table 1. Size distribution analysis of different metal nanoparticles

Material	Average Size (nm)	Size distribution range (nm)
Cu-Al	94	55-145
Al	98	65-165
Cu	134	85-190

**Figure 3.** SEM (a), XRD (b), DLS (c), and EDS (d) analysis of laser ablated Al nanoparticles

3.3 Investigations on Cu nanoparticles synthesized at 532 nm laser wavelength with 50 J/cm² laser fluences:

Laser ablated Cu nanoparticles at 532 nm wavelength with 50 J/cm² fluence is shown in figure 4. SEM image shows the spherical shape, size and surface morphology of as synthesized Cu nanoparticles where particle size distribution was investigated through DLS analysis (figure 4(c)). Average particle size of 134 nm was calculated from DLS analysis. Crystalline formation of Cu nanoparticles with their oxidation behaviour were investigated from XRD and EDS characterizations respectively.

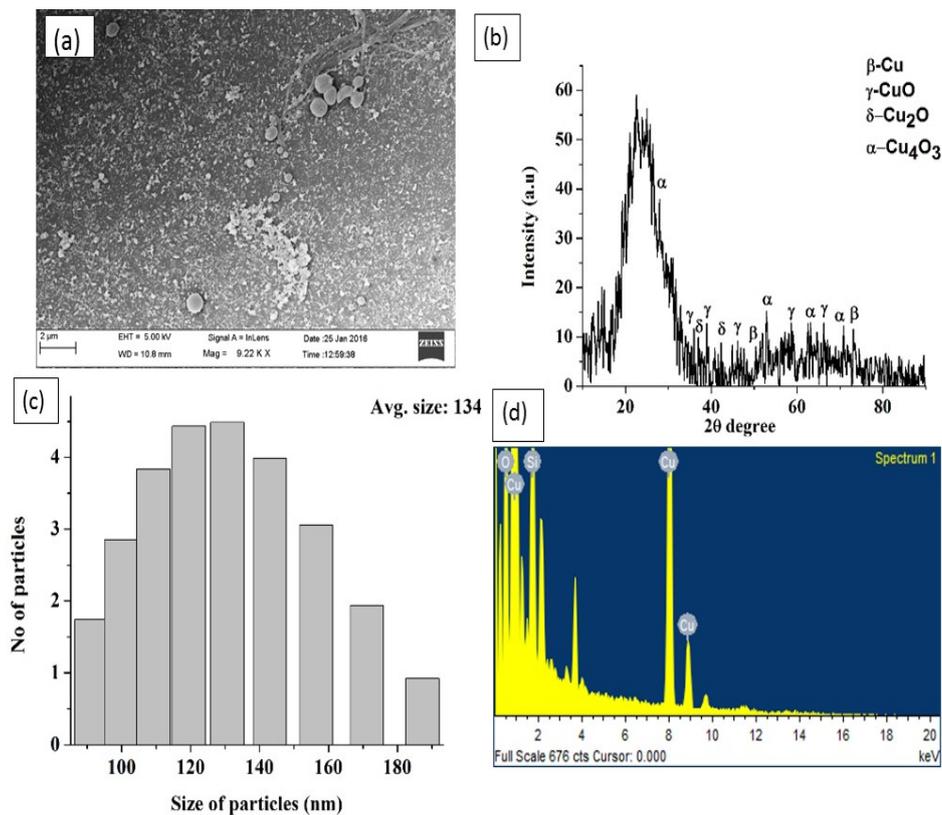


Figure 4. SEM (a), XRD (b), DLS (c), and EDS (d) analysis of laser ablated Cu nanoparticles

Thus, it has been scrutinized from three different DLS graphs, that the particle size is smaller in case of alloy nanoparticle than its monometallic counterparts. The probable reason might be the growth rate of crystallite is slower in case of alloy particles than the pure one [18]. The crystallinity and alloy formation of particles were confirmed from XRD and EDS analysis. Moreover, the oxidation behaviour was observed for all of the metal particles (Cu, Al, and Cu-Al) due to the high oxidation potential.

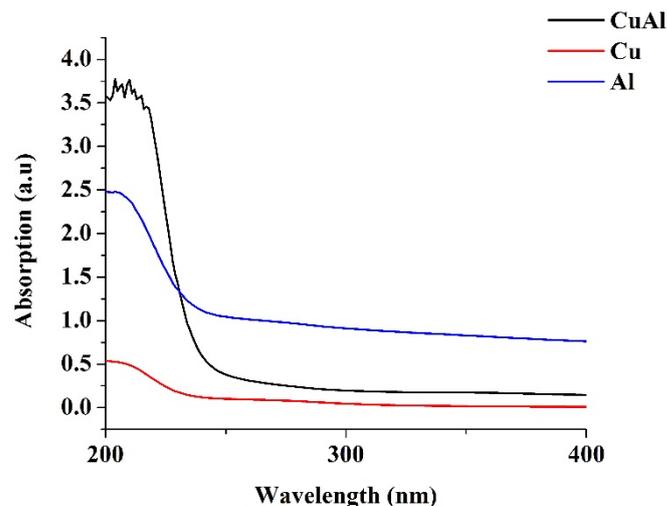


Figure 5. Absorption spectra of Cu-Al, Cu and Al nanoparticles

Furthermore, the optical absorption spectra of three different metal nanoparticles are shown in figure 5. It was evident from spectra that the absorption peak of metal nanoparticles mostly lie in the UV region of spectrum [11, 19]. Though Cu nanoparticle typically shows its absorption in the visible region [10, 11] but the absorption peak of such nanoparticles lies in the UV range owing to their oxidation behaviour. It was also observed that the absorption intensity of alloy nanoparticle is significantly higher than Cu and Al nanoparticles. Hereafter, such high intensity congruent to the nanoparticle concentration in solution. Thus, we can conclude that the ablation rate of alloy nanoparticles was more than the parent materials. Further, we have calculated the bandgaps of different metal nanoparticles from their absorption spectra. Bandgaps around 5.2 eV, 4.8 eV and 4.5 eV were calculated for Cu-Al, Cu and Al nanoparticles respectively. It was evident from the absorption spectra that the band gap of alloy particle is larger than the pure particles.

4. Conclusion:

In summary, we have used earth abundant material (Cu and Al) to generate Cu, Al and CuAl alloy nanoparticles through underwater laser ablation technique. Importantly, the laser synthesis of CuAl alloy nanoparticles have been investigated for the first time in this report. It was observed that the size of alloy particle is much smaller (~90 nm) in comparison to its monometallic particles. Crystalline formations of monometallic and bimetallic particles were verified through XRD whereas the presence of dominating elements was examined through EDS analysis. Hence, the alloy formation of nanoparticles is confirmed from such structural analysis. Herein we can claim that CuAl alloy nanoparticles can be synthesized through underwater laser ablation technique. Moreover, such binary alloy particles show improved optical absorption than monometallic particles. Thus it can be concluded that, alloy nanoparticles with improved optical absorptivity can be achieved through underwater laser ablation technique.

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