Synthesis & characterization of copper nanoparticles using LASIS and chemical reduction technique

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Abstract

Nanotechnology refers to the creation and utilization of material whose constituents exist at the nano scale and by convention is up to 100nm in size. Nanotechnology explores electrical, magnetic and optical activity as well as structural behavior at the molecular and sub molecular level. The control over in particle size and in turn size dependent properties of copper nanoparticles is expected to provide additional applications. Various methods for synthesis of copper nanoparticles have been reported including chemical methods, physical methods, biological methods, and green synthesis. A detailed discussion on the synthesis of copper nanoparticles using LASIS and chemical reduction technique are mentioned and the characterization of synthesized copper nanoparticles is done by UV- Visible spectroscopy using Mie Theory for theoretical particle size estimation.

Keywords: Nanoparticles, Copper Nanoparticles, LASIS, Chemical reduction method, Mie Theory

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1. *Introduction*

A nanoparticle is a particle having sizes less than 100 nm. Unlike nano particles, a bulk material is having a constant physical properties regardless of its size [1, 2]. Due to a wide variety of applications in various fields such as electronic, electrical, optical, and biomedical fields, the nanotechnology is currently an active research area in both physics and chemistry [2, 3]. Nanoparticles are very important as they provide information effectively between bulk materials and atomic or molecular structures [4, 5]. Properties depending on the size of the particles such as quantum confinement, surface Plasmon resonance in some metal particles and super paramagnetism are observed [6-10]. As the size approaches to the nanoscale a significant change in the properties of the material is observed [11, 12]. For bulk materials which are having particle sizes more than one micrometre the percentage of atoms at the surface is minuscule relative to the total number of atoms of the material. The interesting and unexpected properties of nanoparticles are not only partly due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties [13-15]. As compared to bulk material the nanoparticles exhibit a number of special properties. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale [10, 16, 17]. Copper nanoparticles which are smaller than 50 nm are considered to be super hard materials and they don't have the same properties of that of bulk copper [18]. Sometimes a undesirable change in properties also occurs. For example the ferroelectric materials smaller than 10 nm switches their magnetization direction using thermal energy at room temperature which makes them useless for memory storage. Suspensions of nanoparticles are possible due to the interaction of the particle surface with the solvent is strong enough to overcome differences in density, which results in a material either submerged or floating in a liquid [19, 20]. Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects [21-28].

1.1 Theoretical prediction of size of nanoparticles

In the case, when nanoparticles are assumed as uniformly dispersed spherical objects, according to the Mie theory their cross- -section can be calculated from [29]:

$$\sigma(\lambda) = (18\pi V\ Nl\varepsilon^{3/2} m /2.303\lambda)\ (\varepsilon_2 /(\varepsilon_1 + 2\varepsilon_m)^{2} + \varepsilon_2{}^{2}) \ , \qquad (1)$$

where V is the volume of one particle, ε_m dielectric constant of the medium (in our case water), ε_1 and ε_2 real and imaginary parts of dielectric constant of metal ($\varepsilon_1 = n^2 - k^2$; $\varepsilon_2 = 2nk$) and λ wavelength in vacuum. For noble metals Lorentzian shape of absorbance curve is expected with a resonance when the condition $\varepsilon_1 = -2\varepsilon_m$ is satisfied.

For transition metals the Mie theory stands only when neglecting damping constants and interband transitions, which are quite high due to weak interaction of electrons from s and d shells. For accurate SPR determination in transition metals Drude free-electron model is used for metals dielectric constants ε_{D1} (real) and ε_{D2} (imaginary) evaluation, considering relaxation and plasmon frequencies, which are given by expressions

$$\varepsilon_{D1} = 1 - \omega_p{}^2 /(\omega^2 + \gamma^2), \qquad (2)$$

$$\varepsilon_{D2} = \omega_p^2\, \gamma/[\omega(\omega^2 + \gamma^2)], \qquad (3)$$

where ω_p and γ are plasmon and relaxation frequencies, respectively.

Collisions of particles γ can be calculated from:

$$\gamma(r) = \gamma_{bulk} + C\, \upsilon F\, r\ . \qquad (4)$$

Interband dielectric constants are calculated from:

$$\varepsilon_{bulk}(\omega) = \varepsilon_{bound\text{-}electrons}(\omega) + 1 - \omega_p^2\, \omega^2 + i\omega\gamma_{bulk}\ . \qquad (5)$$

2. *Materials Acquired*

Copper nitrate, Polyvinylpyrrolidone (PVP), Hydrazine hydrate and copper plate of thickness of 3 mm all the materials and chemicals were procured from local chemical suppliers. Double distilled water was prepared in our own water distillery system.

3. *Experimental Setups*

1. *Laser Ablation Technique*

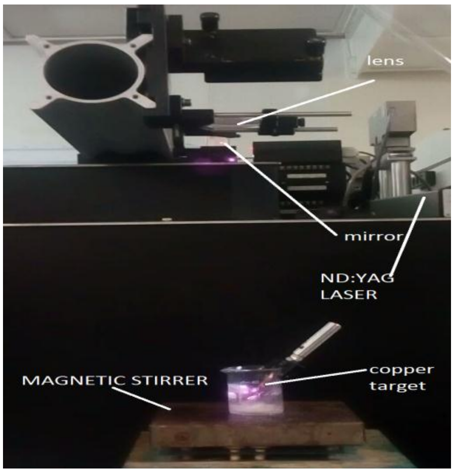

Fig 1. Experimental Setup of LASIS

Laser ablation was in distilled water with a ND: YAG (Continnum Laser, USA) nanosecond laser system with a repetition rate of 30 Hz. The sample was placed in a glass cell filled with distilled water. The laser beam was focused with a lens of 240mm focal length (Newport, USA) at normal incidence on the surface of the copper target. The typical spot dimension at the focal position was 250 ±10 µm. The incident laser fluence was varied by incident laser energy variation and also by laser beam pattern diameter variation. All experiments were carried out at room temperature and atmospheric pressure. UV-Visible spectroscopy was carried out with freshly prepared solution at different irradiation. Fig1 shows the experimental setup for LASIS

2. Chemical Reduction Technique

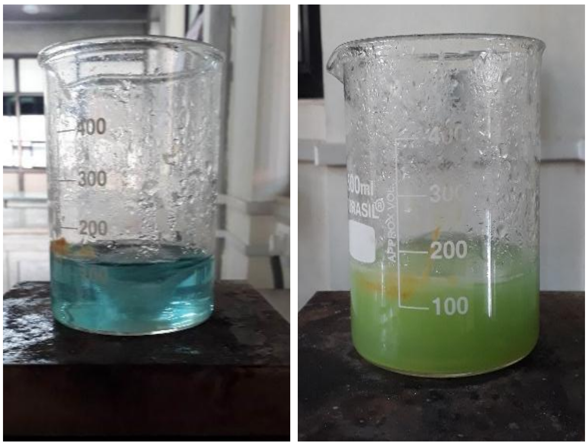

Fig 2. (a) Sky blue color obtained by adding copper nitrate and PVP (b) green color obtained after adding hyrazine hydrate

2gm PolyVinyl-Pyrrolidone (PVP) was slowly added in 100 ml of distilled water and was heated at 60°C with constant stirring for 1 hour until it was dissolved properly. Then 1g copper nitrate was added into the solution and was stirred for another 10 minutes till color change was observed from colorless to sky blue. Then 5% hydrazine hydrate was added drop wise to the solution with vigorous stirring until the color turns to green. The color change from blue to green signifies nanoparticle formation. UV-Visible spectroscopy was carried out with freshly prepared solution. Fig 2 shows the color change of the solution.

4. Result and Discussion

To study the stability of Cu colloidal solution in air, the absorption of Copper-nanoparticles was measured by UV-visible spectroscopy (Shimazdu UV-1700). The absorption bands of copper nanoparticles are reported in the range of 500-600 nm. UV-Visible absorption spectra of Copper nanoparticles by chemical reduction method (CRM) and the solution obtained using LASiS is shown in figure 3.

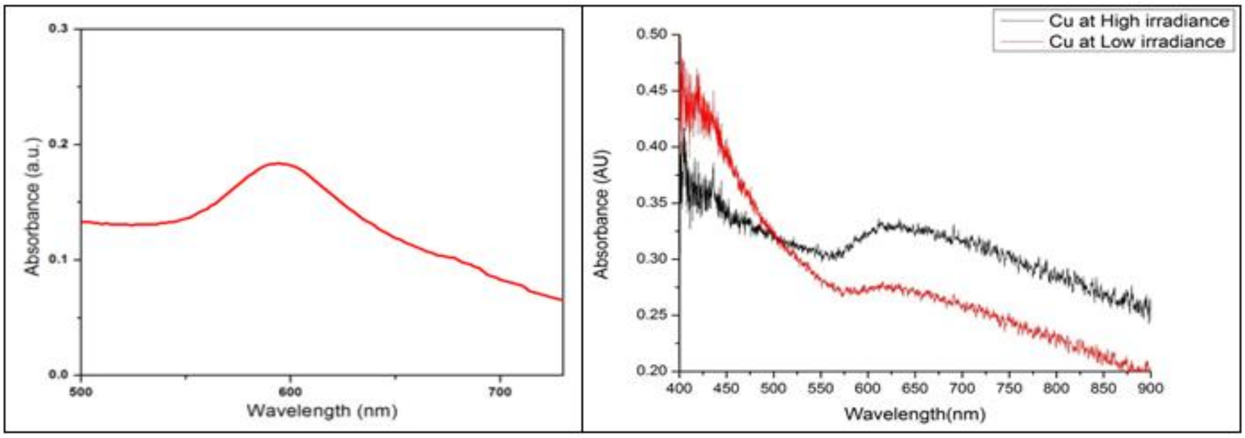

Figure-3: (a) Shows the colloidal copper solution prepared using Chemical Reduction technique (b) Shows the colloidal copper solution prepared using LASIS technique

The spectrums are recorded soon after the synthesis of particles. The figure 3 (a and b) shows the absorption peaks at 577 nm and 612 nm respectively, which confirms the formation of the copper nanoparticles in the solution. A broad band is indicative of wide particle size distribution of copper within the matrix. The intensity and width of the band denote the presence of spherical copper nanoparticles, which also coincides with the Mie theory. Theoretical size evaluation by the Mie approximation model the average diameter of Cu nanoparticles is ≈80-90 nm in case of chemical reduction and for the case of LASIS the average diameters are coming 60-70 nm with an error of ±10-15nm in both the cases.

5. Conclusion

The present study provides information on simple, affordable and significant methods for the synthesis of copper nanoparticles through the reduction of copper salts in aq. medium. An attempt is made to study the absorption phenomenon in copper nanoparticles, due to surface plasmon resonance, which is found to be prominent after 550 nm, and a broad spectrum is found which indicates wide size of the particles. Using the Mie theory, a theoretical particle size was estimated. The future work will be to collect more samples as currently only two samples were acquired, so a solid conclusion cannot be made because of the lack of data. Moreover, we will try to prepare samples using different energies of the Laser and a detailed UV- visible spectroscopy, TEM and XRD will be studied for theoretical and experimental co-relation.

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