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Research Paper

Preparation, Characterization and Stabilization of Nano-sized Copper Particles

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Abstract: *Cu nanoparticles dispersed in water were prepared by the reduction of* Cu^{+2} *originated from the copper salt solution. The stability of the Cu nanoparticles in dispersion was monitored through the analysis of the absorbance spectra at different stages during the process of synthesis. The stability of the Cu nanoparticles dispersed in aqueous medium was investigated after different time intervals. Cu colloid was found to be stable up to 18 hours without major aggregation under atmospheric condition. The size and size distribution of the particles were examined by particle size analyzer. The morphology of the particle synthesised was examined by SEM and AFM. After 24 hours of storage in open air there was some agglomeration of nanoparticles as observed by particle size analyzer and AFM studies. But found stable with the use of 1 % trisodium citrate as stabilizer.*

Keywords*:* Absorbance, Copper, Nanoparticles, Particle size, Plasmon resonance.

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1. Introduction

In recent decades, nanotechnology has attracted scientists from many different areas. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometre range [1, 2]. When a bulk material is divided into small size particles with one or more dimensions (length, width, or thickness) in the nanometre range or even smaller, the individual particles exhibit unexpected properties which are different from those of the bulk material. It is known that atoms and molecules possess totally different behaviour than those of bulk materials; while the properties of the former are described by quantum mechanics, the properties of the latter are governed by classic mechanics. The behaviour of a material changes between these two distinct domains and the nanometre range is considered as the threshold for the transition of a material's behaviour.

Metal nanoparticles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, catalysis, etc. Many metal nano particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase [3]. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nanoparticles is the reduction of metal ions in solution [4, 5, 6]. However, the control of size and shape at the nanometer level is a real problem, as the mechanism of size/shape control is still left largely unresolved.

In this work, an attempt has been made to analyse formation of Cu nanoparticles from copper salt at different stages of synthesis as well as after storing for variable time in atmospheric condition. The effect of time after synthesis on the shape and size of these particles was investigated using Particle size analyzer, SEM and AFM systems. Further, the effect of trisodium citrate as stabilizer for the nano particles was also investigated.

2. Experimental

2.1 Preparation of Cu Colloid

Copper sulphate $CuSO_4$, sodium borohydride $NaBH_4$ and tri-sodium citrate $C_6H_5O_7Na_3$ of analytical grade purity were used without further purification as starting materials.

The copper colloid was prepared using chemical reduction method. The solutions of all the reacting materials were prepared in distilled water. 100 ml of $1 \cdot 10^{-3}$ M $CuSO_4$ solution kept in a specially designed reaction chamber was reduced by drop wise addition of highly dilute and chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction, the solution was stirred vigorously. As the colour of the solution turned to light yellow 5 ml of 1 % trisodium citrate was added drop by drop as stabilizer.

2.2 Analysis Techniques

The absorbance of colloidal solution was recorded at different stages of synthesis using UV-visible spectrophotometer (Shimadzu UV-2450, Japan) in the wavelength range: 300 nm to 700 nm. Particle size and size distribution of the Cu colloid were analyzed using particle size analyzer (Malvern instrument, DTS version 4.20. U.K.), Copper nanoparticles were deposited on carbon coated aluminium sheet and on glass plate for examination in scanning electron microscope (SEM) and atomic force microscope (AFM) respectively. Morphology of Cu nanoparicles deposited on glass plate was examined with an Atomic Force Microscope (easy Scan 2, Nanosurf AG, Switzerland) operating in a contact mode (cantilever force constant 3 N/m). Image processing and analysis of the Scanning Electron Microscopy data was performed on SEM instrument (model JSM5610LV, version 1.0, Jeol, Japan). The synthesized nano particles were also elementally detected on SEM using oxford –Inca software (Oxford, U.K.).

3. Results and Discussion

3.1 Optical Properties of Cu Colloid

Figure 1 (a, b and c) represent the absorption spectra of different stages during the formation of Cu nanoparticle colloid from copper sulphate solution. It is seen from the adjacent photographs of the absorbance curves that a blue green solution of copper sulphate gradually turned to yellow indicating the formation of Cu nanoparticles. The shifting of colour is due to the surface plasmon resonance, with a significant contribution from the interband transition which produces yellow colour hydrosol having maximum absorption at 580 nm (Figure 1 c & d) indicating nano Cu particles generation. The plasmon resonance of Cu nano particles was also observed at near 580 nm by Kazakevich et al [7]. Metals with free electrons possess plasmon resonances in the visible spectrum, which give rise to such intense colours. These properties are mainly observed in Au, Ag, and Cu because of the presence of free conduction electrons. The electric field of the incoming radiation induces the formation of a dipole in the nanoparticle. A restoring force in the nanoparticle tries to compensate for this, resulting in a unique resonance wavelength [8]. The oscillation wavelength depends on a number of factors, among which particle size and shape, as well as the nature of the surrounding medium, are the most important factors [9]. For elemental analysis, the synthesized nanoparticles were deposited on carbon coated aluminium sheet and the particles on the sheet were further coated with gold which was then observed on SEM-Inca instrument. Fig.4 (a) shows the image of this observation and the elemental analysis results presented in Fig. 4(b) confirms the presence of copper particles.

To monitor the stability of the Cu colloid in air, we have measured the absorption of the colloid after different periods of time. The UV-VIS spectrums recorded after different time intervals are shown in Figure 2 (a, b and c). There was no change in peak position for 12 hrs and 18 hrs (Figure 2a and 2b) except for the increase of absorbance. As the particles gain in size, the absorption peak usually shifts towards redder side as we find in Figure 2c. Increase in absorption indicates that the quantity of Cu nanoparticles increased. The stable position of absorbance peak in Figure 2a and 2b indicates that new particles do not aggregate. During the initial trial experiments when Cu nanoparticles were synthesized without the addition of trisodium citrate, the yellow colour of the solution was persisted for few hours only in atmospheric condition. Therefore, trisodium citrate was introduced into the system as a stabilizer. Since the Cu colloidal particles possessed a negative charge due to the adsorbed citrate ions, a repulsive force worked along the particles and prevented further aggregation. But after storing for 24 hrs or more in atmospheric condition the wavelength for maximum absorbance was found to be slightly shifted towards redder side which indicates aggregation of the particles even after the addition of citrate anions. However the scanning electron micrographs (SEM) of Cu nanoparticles (Fig. 5) evident that the average size of the synthesized and citrate anions stabilized nano particles was below 100nm even after 4 weeks.

The particle size distributions of the freshly prepared nano Cu colloid and after storing for 24 hours (Fig 3a & Fig 3b) in atmospheric condition were analyzed on Malvern instrument. It is seen that the size of the majority of the nanoparticles when prepared fresh was about 70 nm but after storage for 24 hours the same was increased to about 400 nm. This is due to the aggregation of nanoparticles which resulted a broadening of peak in Fig.3b.

Stability of the nano Cu particles synthesised in absence of tri-sodium citrate was not satisfactory as observed from the rapid change in colour of the yellow coloured solution. AFM pictures of freshly prepared Cu nano particles and after storing for 24 hours in air are represented in Fig. 6. From the AFM pictures we can see that the size of nanoparticles is slightly increased, after 24 hours. However, when tri-sodium citrate was used, the particle size was controlled up to 4 weeks, which is also supported by the scanning electron micrographs of Cu nanoparticles (Fig. 5 a & b). Cu nanoparticles because of their high reactivity tend to form aggregates. The tendency of getting aggregated was controlled by the citrate anions.

4. Conclusions

Nano Cu colloids were successfully prepared, by reducing Cu^{+2}, using chemical bath deposition technique. The absorbance spectrum of the solution was determined at different stages of the synthesis process. The plasmon resonance absorbance of yellow coloured nano colloids was noticed at 580 nm. These particles were elementally detected by SEM-inca software. The particle size and their distribution, of freshly prepared system and after storing for 24 hours in atmospheric condition, were examined by particle size analyzer shows that the maximum size of the particle was increased from 70 nm to 400 nm during storage for 24 hours. The stability of the particles was improved by the introduction of citrate anions in the colloidal system. Addition of citrate anions resists major agglomeration of particles.

Figures

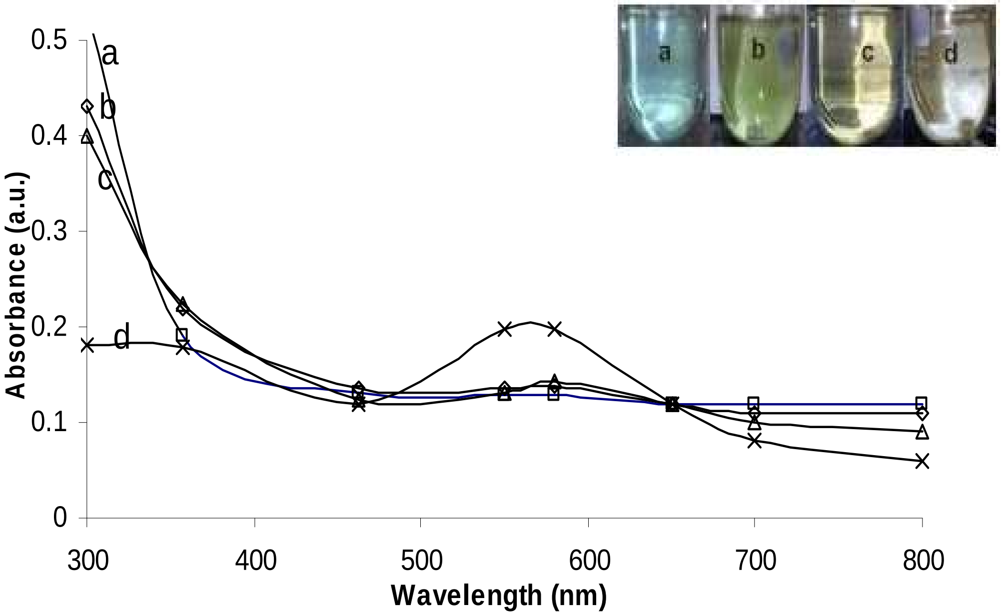

Fig. 1 The UV-VIS spectrums of Cu nano colloids at different stages of synthesis [(a) Stage 1: Cu salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Cu nano colloids and (d) Stage4: stabilized Cu nano colloids.]

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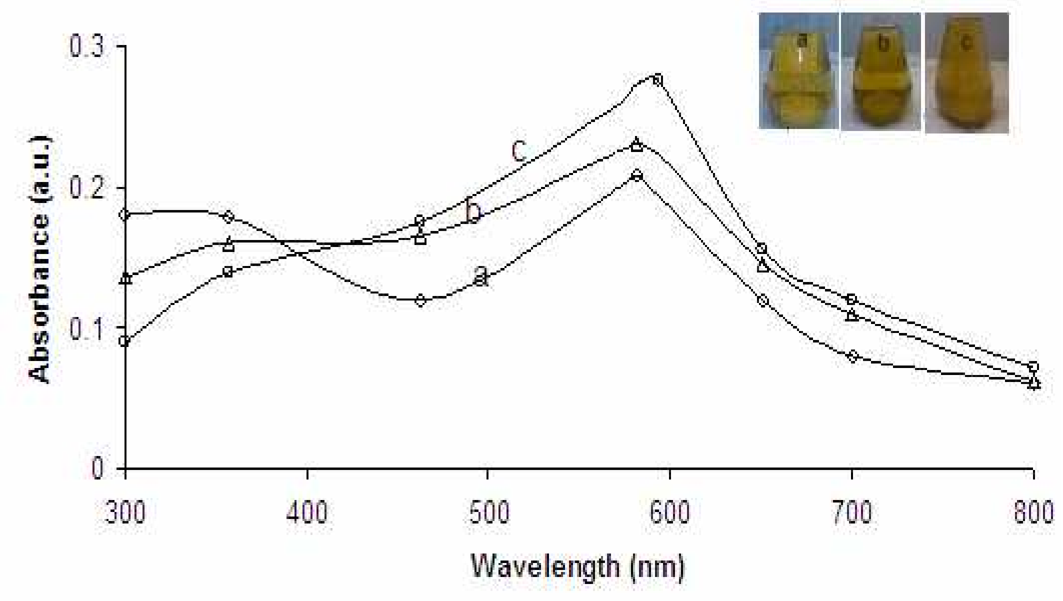


Fig. 2 UV-VIS spectra of Cu nano colloids [Time after synthesis: (a) 12 hours, (b) 18 hours and (c) 24 hours]

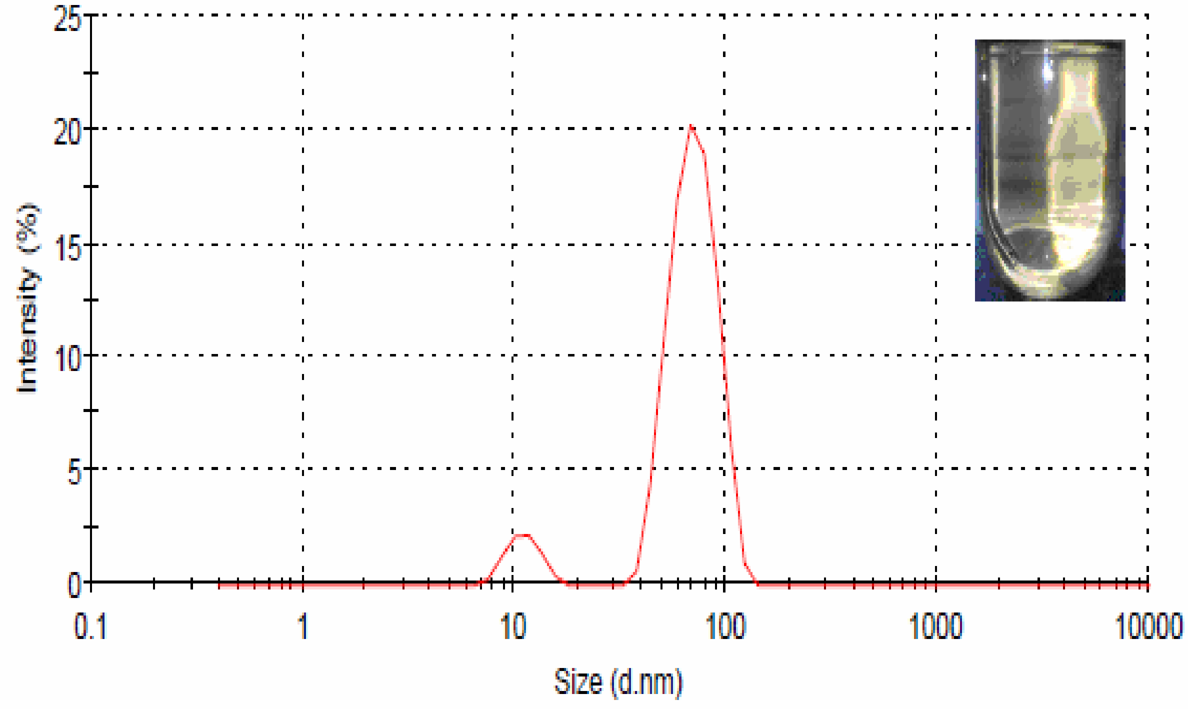


Fig. 3 (a) Particles Size and their distribution for freshly prepared Cu nano colloids

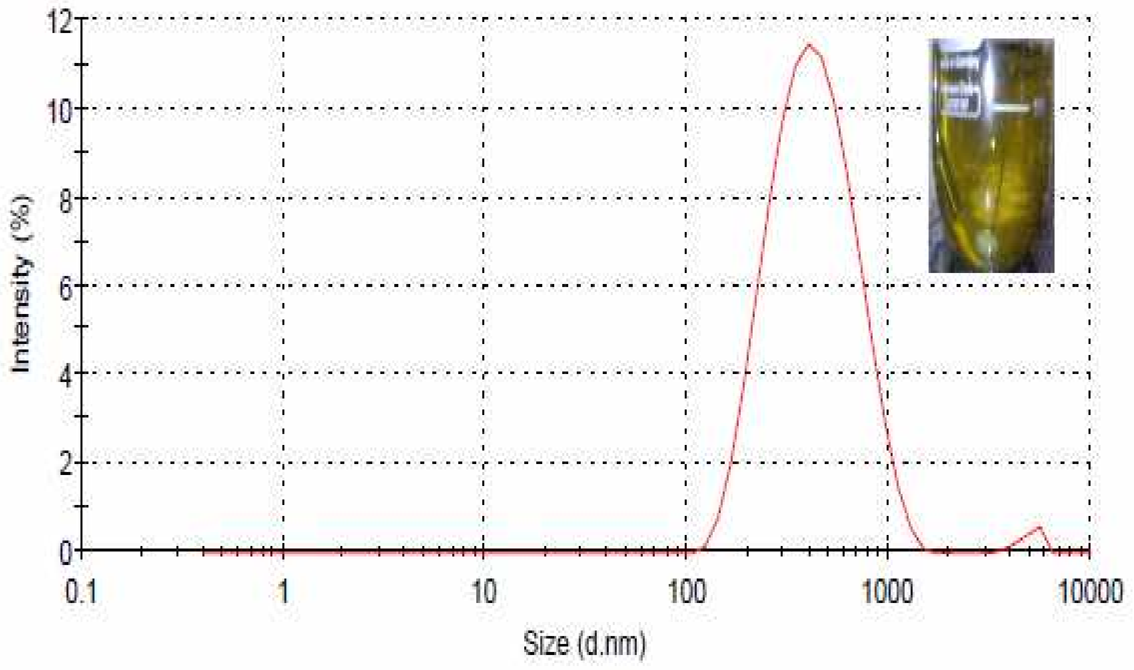


Fig. 3 (b) Particles Size and their distribution after storing for 24 hours

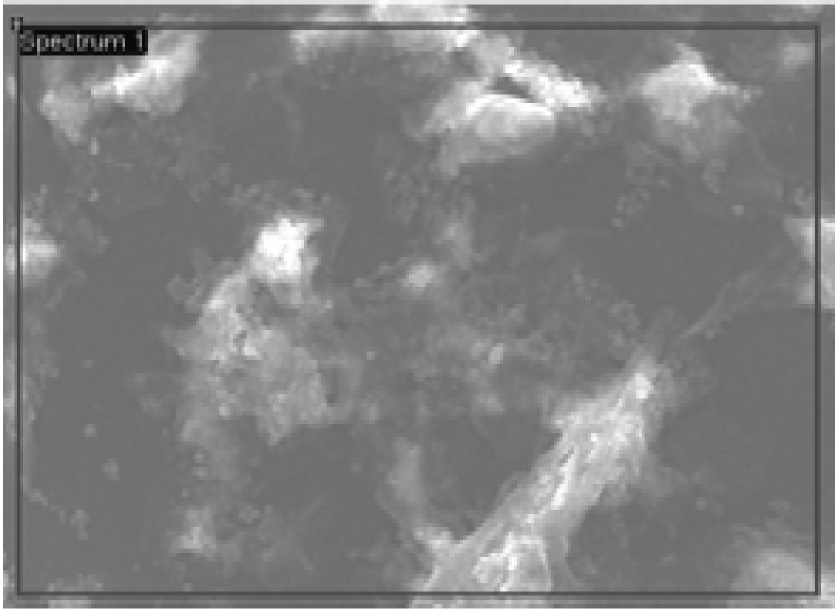


Fig. 4 (a) Selected area of gold coated Cu nano particles for SEM – Inca elemental analysis

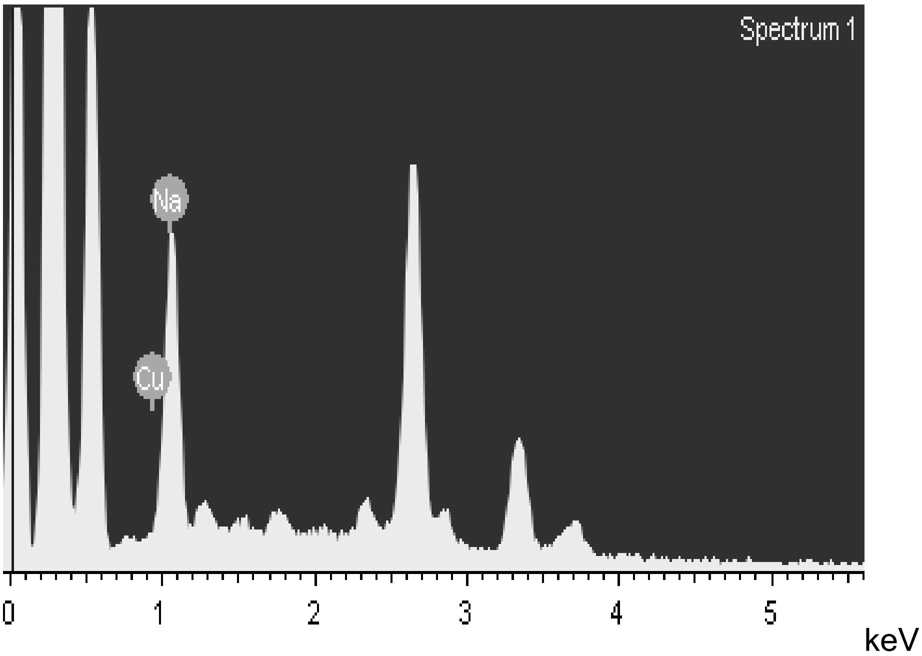
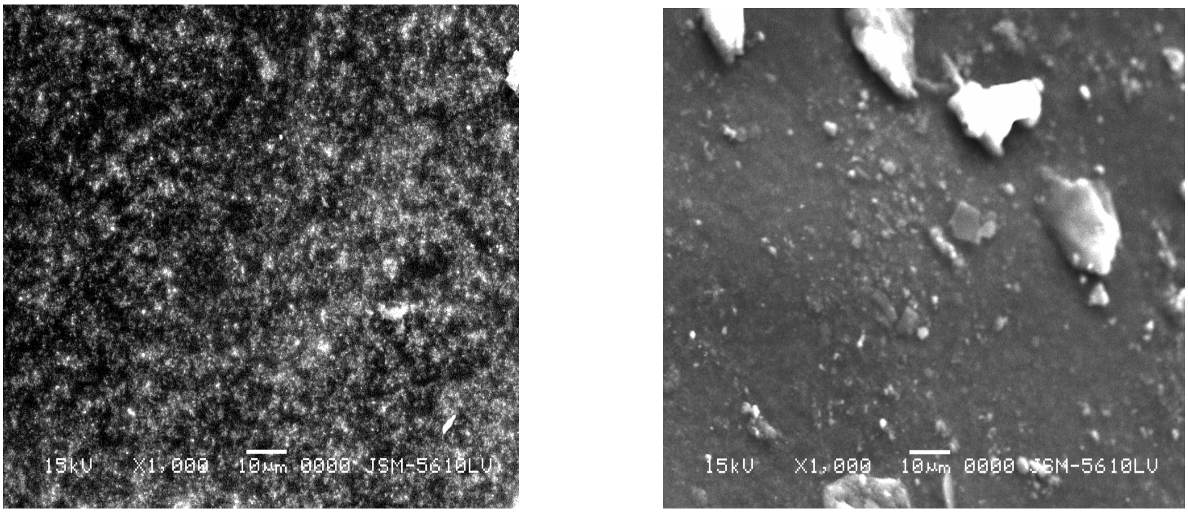
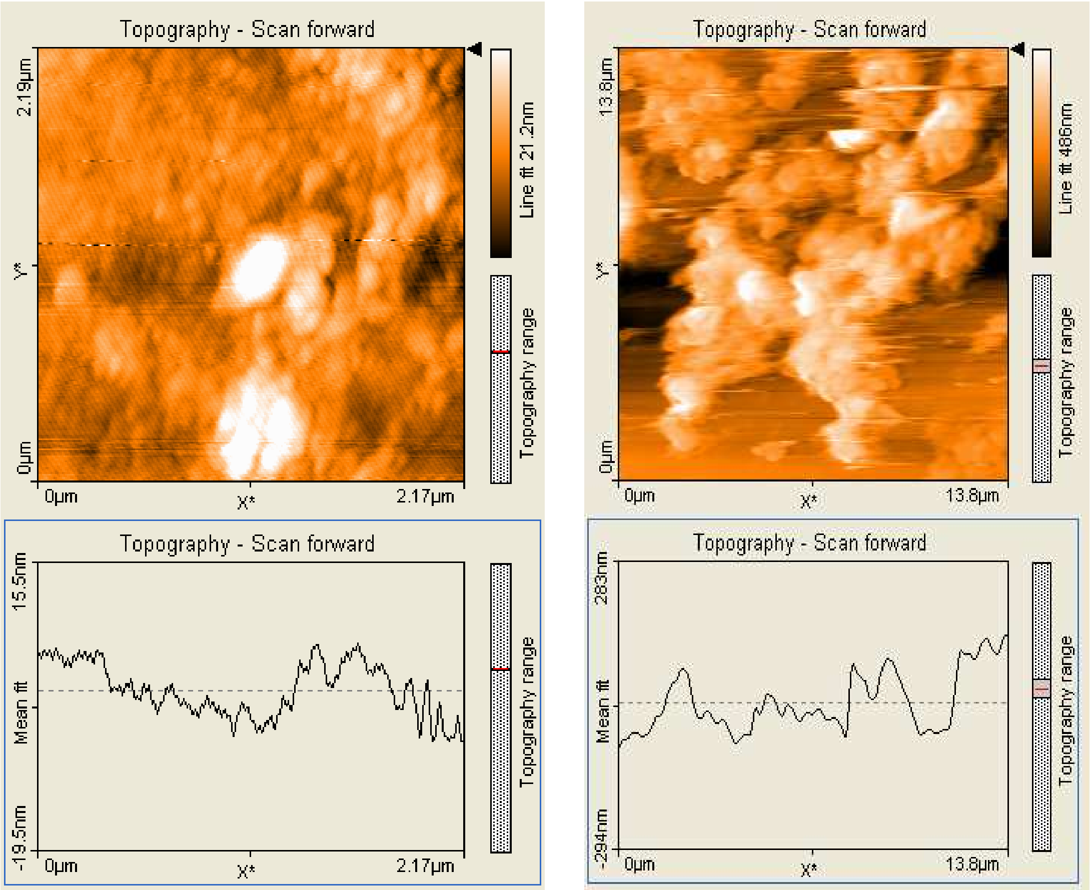


Fig. 4 (b) Elemental analysis of the synthesised particles using Inca software



(a) **(b)**

Fig.5 Scanning Electron Microscope (SEM) images of synthesised copper nano particles [(a) freshly prepared ; (b) after 4 weeks of synthesis]



(a) (b)

Fig. 6 (a) Atomic force microscopic image of freshly prepared Cu nano colloids and (b) After storing over 24 hrs

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