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Nano metal particles: Synthesis, characterization and application to textiles

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Introduction

In recent decades, nanotechnology has attracted scientists from many different fields. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range, as reported by Chattopadhyay, 2006 and Patel & Chattopadhyay, 2007 [1-2]. When a bulk material is divided into small size particles with one or more dimensions (length, width, or thickness) in the nanometer range or even smaller, the individual particles exhibit unexpected properties which are different from those of the bulk material. Metal nano-particles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, catalysis, etc. The optical properties of small metal nano-particles are dominated by the collective oscillation of conduction electrons resulting from the interaction with electromagnetic radiation. These properties are mainly observed in Au, Ag, and Cu, because of the presence of free conduction electrons. Such particles are under active research because they possess interesting physical properties differing considerably from that of the bulk phase as reported by Chattopadhyay and Patel, 2009 [3]. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nano-particles is the reduction of metal ions in solution as reported by Chattopadhyay and Patel, 2009, 2010 and Jana, Wang and Sau, 2000 [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.

Attempts have been made to develop a simple method for synthesizing metal nano-particles of Copper, Silver and Zinc in colloidal solution form. Metallic nano-particles were prepared in aqueous solution by chemical reduction method using sodium borohydride as reducing agent. The metallic nano particles produced was either immediately capped with sodium lauryl sulphate (SLS) or trisodium citrate (TSC). The stability of nano-particles in the dispersion was monitored through the analysis of absorbance spectra at different stages during the process of synthesis. The stability of the nano-particles dispersed in aqueous medium was also examined at different time intervals. Their stability was examined in presence of various capping agents used. The size and size distribution of the particles were investigated by particle size analyzer. The morphology of the particles synthesized was examined by particle size analyzer and atomic force microscope (AFM) studies. A novel in-situ stabilization (i.e. the particles were formed and stabilized in-situ in fiber matrix itself) technique has also been developed and analyzed.

Materials

Various chemicals and material used for the study are listed in Table 7.1 and 7.2. The polyester fabric supplied by Kiran Threads, Vapi (Gujarat) was mild scoured (5% soap Lisaapol L, and 2% soda ash at boil for 15 min.) and thoroughly washed with distilled water before use.

TABLE 7.1

Chemical specification

Name	Formula	Grade	Mol.wt. gm/mol	Supplier
Copper sulphate	CuSO ₄ .5H ₂ O	AR	249.68	Sd Fine chemicals.
Silver sulphate	AgSO ₄ .5H ₂ O	AR	311.80	Sd Fine chemicals.
Zinc nitrate	Zn (NO ₃) ₂ .6H ₂ O	AR	297.47	Sd Fine chemicals.
Sodium borohydride	NaBH ₄	AR	37.83	Sd Fine chemicals.
Tri-sodium citrate	C ₆ H ₅ Na ₃ O ₇ .2H ₂ O	AR	294.10	Sd Fine chemicals.
Sodium lauryl sulphate	CH ₃ (CH ₂) ₁₁ OSO ₃ Na	AR	288.38	Qualigens Fine Chemicals
Lissapol L	-	LR	284	Suvidhenath Chemicals

TABLE 7.2

Polyester material specifications

Sample	Material Specification						
	Count/Denier						
	Warp	Weft	Ends/inch	Pick/inch	Type weave	Wt.gm/sq.m.	Thickness (mm)
100% polyester	128d	146d	90	72	Plain	109.7	0.21

Equipments

Three metallic nanoparticles namely, Cu, Ag and Zn in colloidal form were synthesized by chemical reduction technique. For the synthesis and characterization of these nano particles various equipments were used. Name and make of the equipments are listed below.

- Reaction Chamber (In-house designed) with N₂ gas supply unit and high speed magnetic stirrer as shown in figure 7.1.
- Laboratory two bowl padding mangle: (EEC Pvt. Ltd., Mumbai).
- Spectrophotometer (interphased with computer colour matching system): Spectra scan 5100 (RT) (Premier color scan instrument), India.
- SEM/EDX Model JSM-5610 LV Japan, with oxford Inca Software for characterizing surface morphology and elemental analysis of nano particles,
- UV-VIS Spectrophotometer (Shimadzu UV-2450, Japan): for determining absorbance of nano colloidal solution
- Particle Size analyzer: MAL 501131, DTS version UK, Malvern Instrument was used for analysis the particle size.
- AFM; Easy Scan 2, Nanosurf AG, Switzerland, was used to examine morphology of nanoparticles deposited on glass plate.

- X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan); for quantitative and qualitative elemental analysis of the polymer nano composite materials.

Reaction chamber

The reaction chamber designed and used for the synthesis of nano particles and the schematic animated model of the same is shown in figure 7.1. As seen in the figure, the experiment setup consists of the actual reaction chamber, nitrogen gas supply unit with pressure gauge, magnetic stirrer and stainless steel clamp.

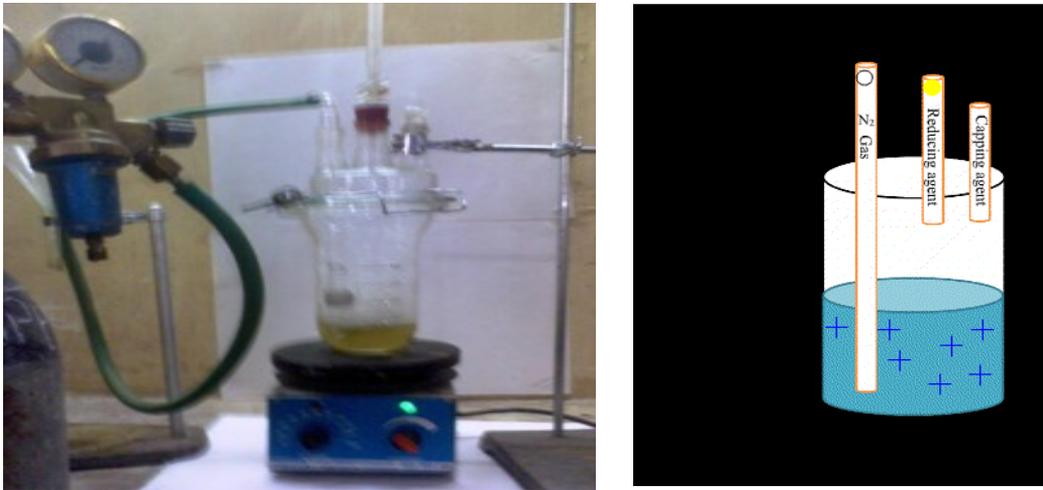


FIGURE 7.1

Experimental setup and schematic presentation; reaction chamber with N₂ gas supply

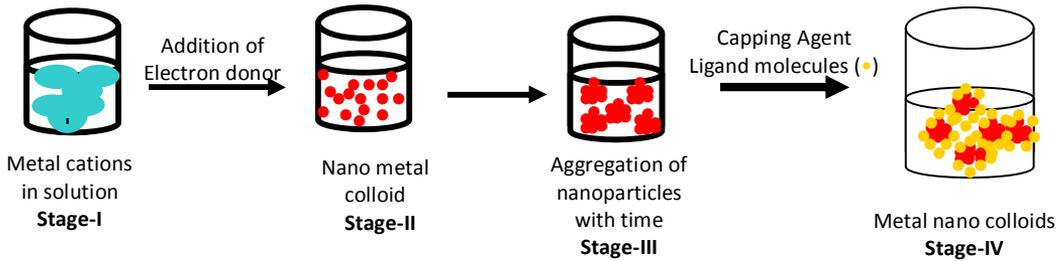
The reaction chamber was made of toughened glass with a capacity of 500 ml. The glass chamber was equipped with three inlets. One for the introduction of nitrogen gas in the reaction mixture, the constant pressure of the nitrogen gas was ensured and monitored through the pressure gauge. Other inlet contains burette along with knob for the insertion of reducing agent inside the chamber. The third inlet was for the insertion of capping agent but initially it was kept closed. The reaction chamber was placed on magnetic stirrer, which ensures constant stirring throughout the experiment. The chamber was kept erect on the magnetic stirrer with the help of clamp.

Experimental methods

Preparation of copper nano colloids by chemical reduction technique

Copper nanoparticles were prepared in aqueous solution by chemical reduction technique using sodium borohydride as reducing agent to reduce copper sulphate to metallic nano copper [5]. In a typical set, 100 ml of 1×10^{-3} M CuSO₄ (CuSO₄·5H₂O, 0.3 gm, 4.17 mmol in 100ml water) solution was purged with N₂ gas for 10 min to remove the dissolved oxygen. 10 ml of 2×10^{-3} M aqueous solution of sodium borohydride (NaBH₄, 0.1gm, 3.83 mmol in 50ml water) was then added drop wise to it under

constant stirring in nitrogen atmosphere. The colour of the solution was changed to dark yellow on gradual addition of reducing agent indicating the formation of copper nanoparticles. 10 ml of (1×10^{-3} M) sodium lauryl sulphate or tri-sodium citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$, 0.1gm, 29.41mmol in 100ml water) was added and allowed to stir for another 10 min for capping of the nanoparticles. Distilled water was used for preparing the solutions of all the chemicals. Scheme 1 gives schematic presentation of Cu nano particle formation and their stabilization by capping agent. The absorbance of nano colloidal solution was recorded using UV-visible spectrophotometer at different stages of synthesis.



SCHEME 1

Schematic process diagram of synthesis

Stabilization study of copper nano particles

The stability of copper nano colloid in absence of capping agent at different time intervals viz, after 12 hrs, 24 hrs 72 hrs and 4 weeks was examined by monitoring its absorbance in UV-VIS spectrophotometer. The effect of time after synthesis on the shape and size of these particles were investigated using particle size analyzer, SEM and AFM systems. Further, the effect of capping agents on the stability of nano particles were studied using two types of stabilizers viz. sodium lauryl sulphate and tri-sodium citrate.

Finally, a novel in-situ synthesis and stabilization technique was adopted i.e. the particles were formed and stabilized in-situ within the fibre matrix itself.

In situ synthesis and stabilization

The cleaned (100%) polyester fabric was used for this experiment. The fabric was first padded with chilled 2×10^{-3} M reducing agent (sodium borohydride solution) using 2-dip-2-nip padding technique at 70% padding expression at room temperature on laboratory two bowl padding mangle. The wet fabric was then further padded with 1×10^{-3} M copper salt ($CuSO_4$) solution using again 2-dip-2-nip padding technique. Finally, the fabric is cured in the curing chamber at $180^\circ C$ for 60 seconds.

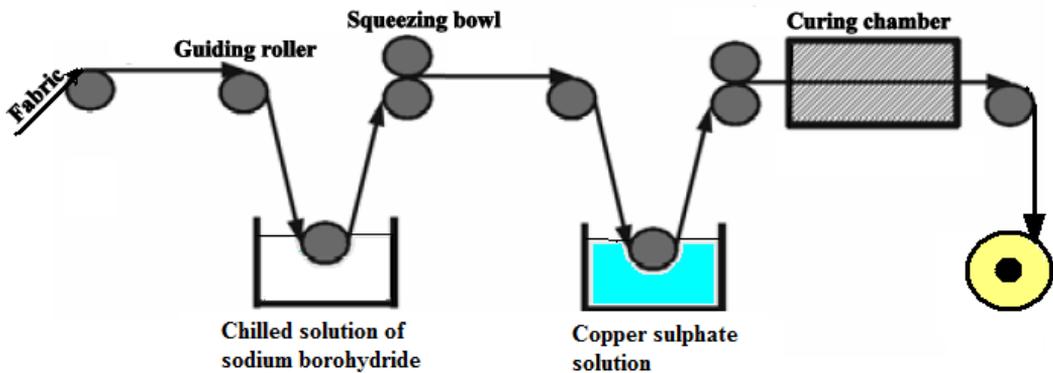


FIGURE 7.2

Schematic process design for in situ synthesis of metallic nano on textile

Preparation of silver nano colloids by chemical reduction

Metallic silver colloids were first prepared over a century ago. Ag nanoparticles can be synthesized using various methods, such as chemical, electrochemical, γ -radiation, photochemical, laser ablation, etc. [7,8]. Silver nano is a trademark name of an antibacterial technology which uses silver nanoparticles in washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners. Antimicrobial effect of silver nanoparticles on textiles has already been shown by various researchers [9,13].

In this study silver nano colloidal solution was prepared by using chemical reduction technique [3]. The 100 ml solution of 1×10^{-3} M AgSO_4 , kept in the earlier discussed reaction chamber (Figure 7.1), was slowly reduced by drop-wise addition of very dilute chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously with the help of magnetic stirrer. When the colour of the solution turned to light yellow, 5 ml of 1×10^{-3} M trisodium citrate were added drop by drop with constant stirring. Distilled water was used for preparing the solutions of all the chemicals.

Stabilization study of silver nano colloidal particles

The formation of Ag nanoparticles from silver salt at different stages of synthesis as well as their stability after storing for variable time in atmospheric condition has been monitored using UV-VIS spectrophotometer. Stability of synthesized Ag nano colloid in air (in absence of capping agents) was recorded at different time intervals i.e. after 12 hrs, 24 hrs 72 hrs and 4 weeks. The effect of capping agents on the stability of Ag nano colloidal particles was studied using TSC (Electrostatic stabilization).

In-situ synthesis and stabilization

The cleaned polyester fabric was used for this experiment. The fabric was first padded with chilled 2×10^{-3} M reducing agent (sodium borohydride solution) using 2-dip-2-nip padding technique at 70% padding expression at room temperature on laboratory two bowl padding mangle. The wet fabric was

then further padded with 1×10^{-3} M silver salt (AgSO_4) solution using again 2-dip-2-nip padding technique

Finally, the fabric is cured in the curing chamber at 180°C for 60 seconds. The fabric samples were thoroughly washed.

Preparation of zinc nano colloids by chemical reduction

Recently, numbers of work have been reported on the developments of nano sized materials and their effect. Havaneak, (2003) [14]; Efras and Rosen (2003) [15] has reported that most of the novel devices of the future will be based on properties of nanomaterials [16]. Furthermore, Dutta and Sugunan (2004) [17]; Gates et.al (2004) [18] has also mentioned that the traditional approaches is not sufficient to achieve size selective nano particles. Various techniques of nano synthesis has been reported in literature, in case of preparation of zinc nano particles, controlled precipitation from precursor dissolved in a solution is most popular.

Zinc nano particles were prepared by wet chemical method as described by Chattopadhyay and Patel 2011, elsewhere [4].

Stabilization study of zinc nano colloidal particles

The synthesized Zn nano colloidal particles (in absence of capping agent) has been monitored with computer colour matching system after storing for variable time in atmospheric condition. Stability of synthesized Zn nano colloid in air was recorded after different time intervals i.e. freshly prepared, after storing for 48 hrs and after storing for 72 hrs, without capping.

In-situ synthesis and stabilization

100 % polyester fabric samples were impregnated and padded with very dilute chilled solution of 2×10^{-3} M sodium borohydride (NaBH_4 , M.W. 37.83, 0.1gm, in 50 ml water) using automatic padding mangle using 2-dip-2-nip padding technique at 70% padding expression on laboratory two bowl padding mangle. The wet sample was further padded with the solution of 1×10^{-3} M Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, M.W. 297.47) using 2-dip-2-nip padding technique (Figure 7.3). The padded substrates were air dried and finally cured at 180°C for 60 seconds in curing oven. The fabric samples were thoroughly washed.

Characterization of prepared nano metal particles

UV-visible spectrophotometry

The absorbance of nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range: 300 nm to 700 nm.

Particle size analyzer

The particle size and size distribution of Cu nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was used to characterize the nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to 100Å°. Stabilized solution of copper nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

Elemental analysis by Oxford-Inca software on SEM

The elemental analysis of the synthesized copper nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The copper nano particles were deposited on carbon coated aluminum sheet and further coated with gold. EDX analysis of these samples was carried out using Oxford-Inca software on scanning electron microscope. The instrument reports the presence of elements in pure and oxide state qualitatively.

Atomic Force Microscopy (AFM)

Morphology of Cu nanoparticles deposited on glass plate was examined with the help of AFM operated in a contact mode (cantilever force constant 3 N/m).

Determination of colour of the colloidal solution

The changes in colour of the colloidal solution were examined and recorded using spectrophotometer interfaced with computer colour matching system.

X-Ray fluorescence spectroscopy (EDX)

For the elemental analysis of polyester fabric before and after in-situ generation of copper nano technique were performed by X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.

Results and Discussion

This section interprets the findings on synthesis, characterization and stabilization of copper, silver and zinc nano particle.

Synthesis of colloidal copper nano particles

Copper nano particles were prepared by chemical reduction of copper salt. The change in colour of the copper sulphate solution was captured at different stages during synthesis of copper nano colloid. Figure 7.3 shows how the blue-green colour of the copper sulphate solution gradually changed at different stages during synthesis. The optical properties of metal nanoparticles depend strongly upon the particle size and shape as reported by Mulvaney, 1996 [19]. The formation of nano sized Cu was noticed by the change in the optical properties of the reaction solution. The blue-green colours of

CuSO_4 solution gradually change to intense yellow when the particle size of copper was reduced to nano level. The Cu nano particles in the solution were analyzed by particle size analyzer. The particles were also observed using SEM and AFM. The presence of Cu was detected by Energy dispersive X-ray spectroscopy (EDX).

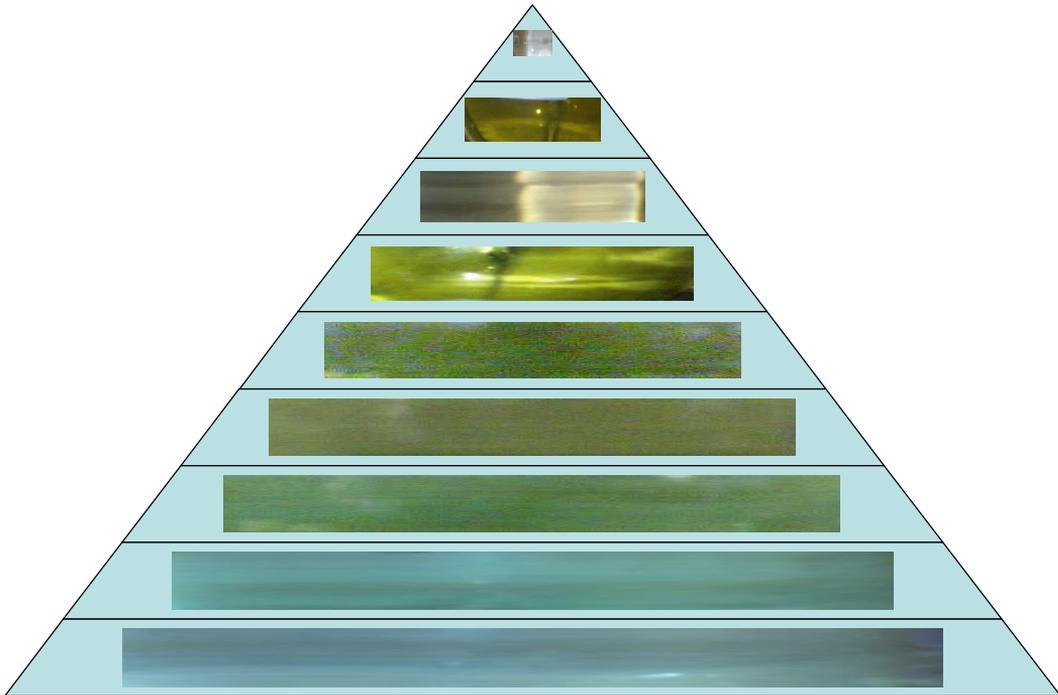


FIGURE 7.3

Progressive colour change of copper sulphate solution during the preparation of copper nano particles

Stability of copper nano colloidal solution in atmospheric condition

The stability of the copper nano colloid in absence of any capping agent stored for 24 hours in atmospheric condition was examined using particle size analyzer, SEM and AFM. The results are compared with the results of the freshly prepared copper nano colloid kept in similar environment and detailed by Chattopadhyay and Patel, 2012 [20]. Particle size analysis gives an idea of the changes in size and size distribution of the particle with time. Nano particles are prone to cluster with time. The specialities of the nano particles are associated to its size. With increases in size its specialities also get reduced and after a certain point it starts behaving like normal (bulk) metal atoms. It is seen from the figure 7.4(a) and 7.4(b) 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 as seen in Figure 7.4 b. The inset photographs show the change in colour.

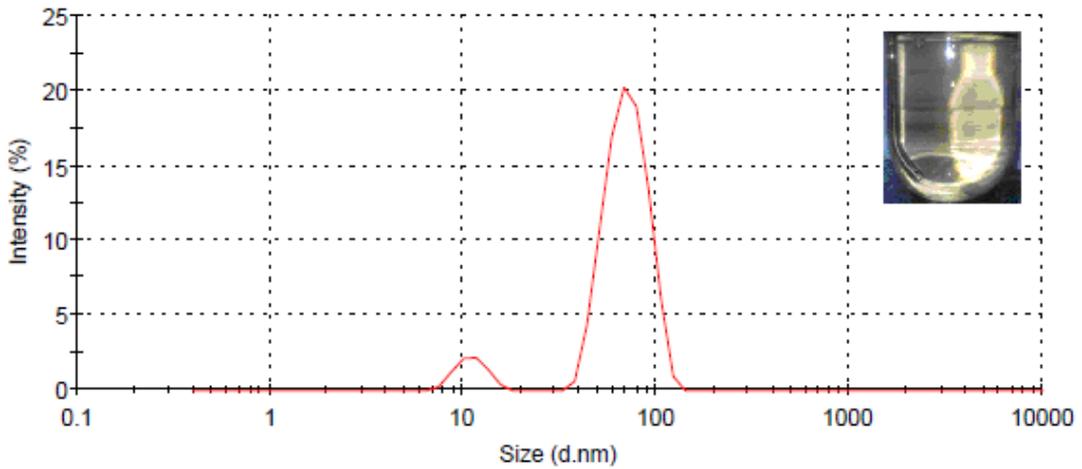


FIGURE 7.4
 (a) Particles Size and their distribution for freshly prepared Cu nano colloids [20]

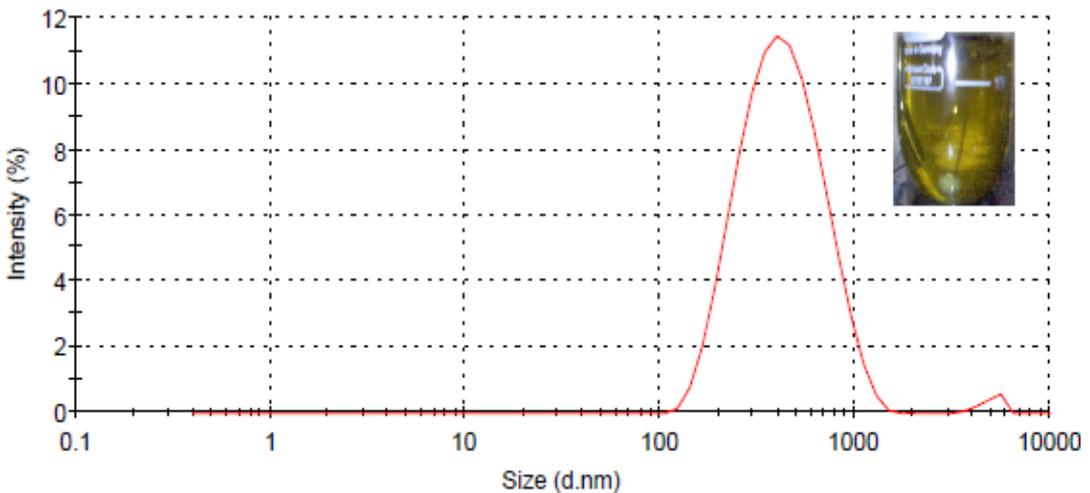


FIGURE 7.4
 (b) Particles Size and their distribution after storing for 24 hours [20]

Stability of the nano Cu particles colloid (in absence of capping agents) in atmosphere was not satisfactory as observed from the change in colour. Scanning electron micrographs of freshly prepared Cu nano particles and after storing for 24 hours in air are represented in figure 7.5. From the SEM photograph we can see that the size of nanoparticles is increased, after 24 hours, which is also supported by the atomic force microscopic images presented in figure 7.6.

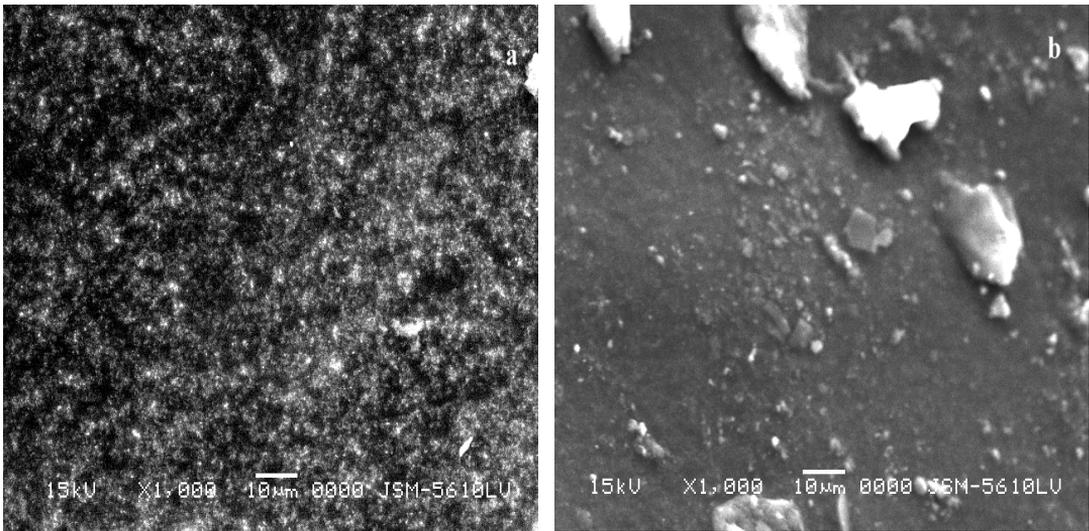


FIGURE 7.5

Scanning Electron Microscope (SEM) images of synthesized copper nano particles [(a) Freshly prepared; (b) After 4 week of Synthesis] [20]

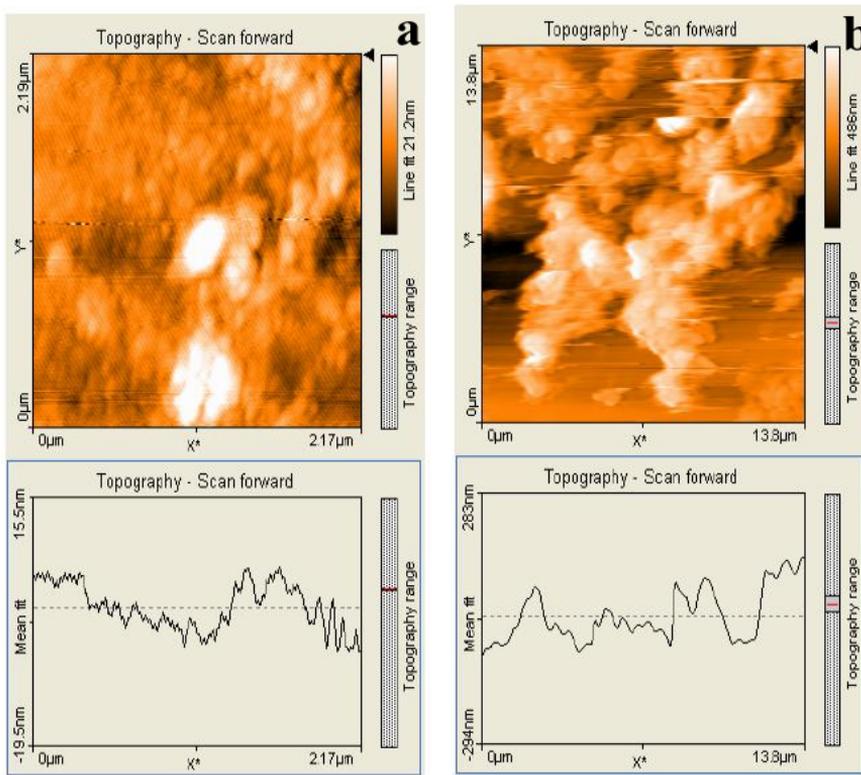


FIGURE 7.6

(a) Atomic force microscopic image of freshly prepared Cu nano colloids and (b) After storing over 24 hrs. [20]

Cu nanoparticles because of their high reactivity tend to form aggregates. The tendency of getting aggregated was therefore controlled by the stabilizer or capping agents reported in the following section.

Stability with different capping agents

We have seen in the previous section that the stability of copper nano colloid get affected with time. It was found that even after 24 hours the size of the particles, ranged between 200-1000 nm due to aggregation (Figure 7.4). To enhance the stability of the copper nano colloid two methods of stabilizations were investigated i.e. Steric Stabilization (SLS) and Electrostatic stabilization (TSC).

Effect of Steric Stabilization (SLS)

During the synthesis of copper nano particles as the colour of solution change to yellow the Cu nano colloidal particles were stabilized with the addition of Sodium Lauryl Sulphate (SLS) (1×10^{-3} M). In the present experiment the steric stabilization of colloidal particles was achieved by attaching SLS macromolecules to the surfaces of the copper nano particles.

To check the efficiency of SLS as stabilizing agent for Cu nano colloid, we have examined and recorded the variation of colour of the SLS stabilized Cu nano colloids at different time intervals using computer colour matching system (CCM). The results recorded at different time intervals are shown in figure 7.7. There was no significance change in colour up to 48 hrs, but after that the colour changed to light green and further storing for 72 hrs the colour was changed to greener blue. The steric stabilization was thus not found to be very effective in arresting particle aggregation for a longer time as evaluated from the change in colour of the copper nano colloid with time.

Colour Difference

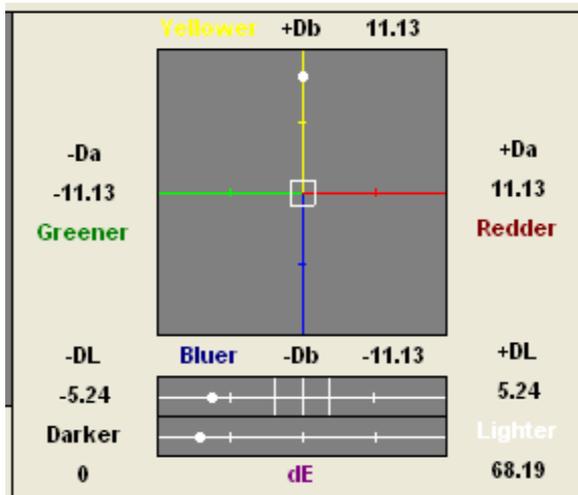
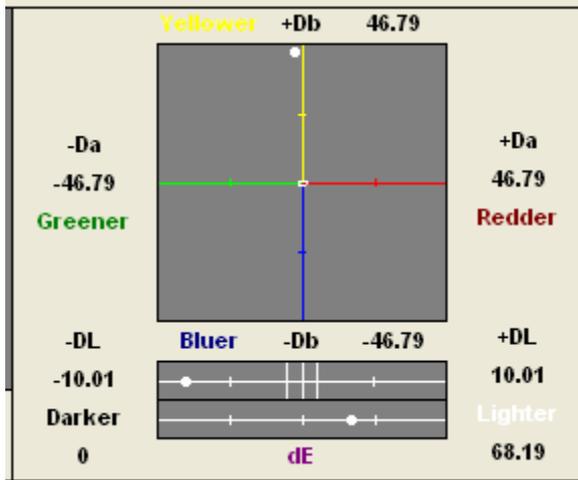


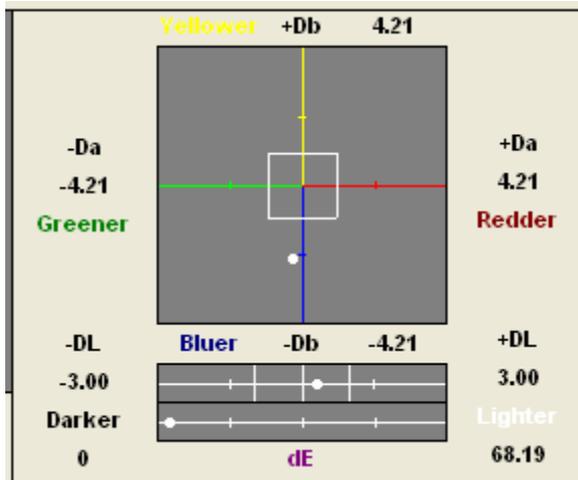
Image at time interval



SLS Stabilized Cu nano (Fresh)



SLS Stabilized Cu nano (After 48 hrs)



SLS Stabilized Cu nano (After 72 hrs)

FIGURE 7.7

Change in colour of the SLS stabilized Cu nano colloidal solution on storage in atmospheric condition for different time intervals

Effect of Electrostatic stabilization (TSC)

Figure 7.8 shows the colour difference and actual photographs of the TSC stabilized freshly prepared copper nano colloid and stored for 72 hours and 4 weeks. From the figure it is seen that in contrast to SLS stabilized solution the colour of the TSC stabilized copper stored for 72 hours is more yellowish which indicates a better stabilization in the latter case.

Colour Difference

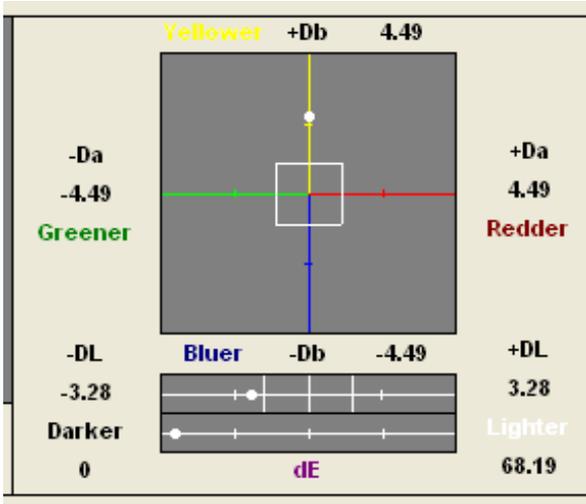
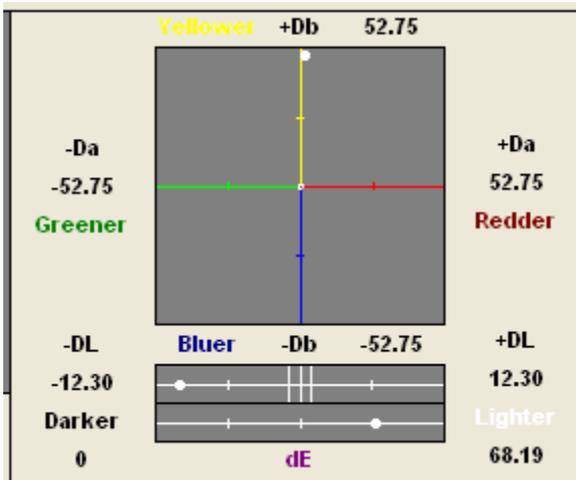


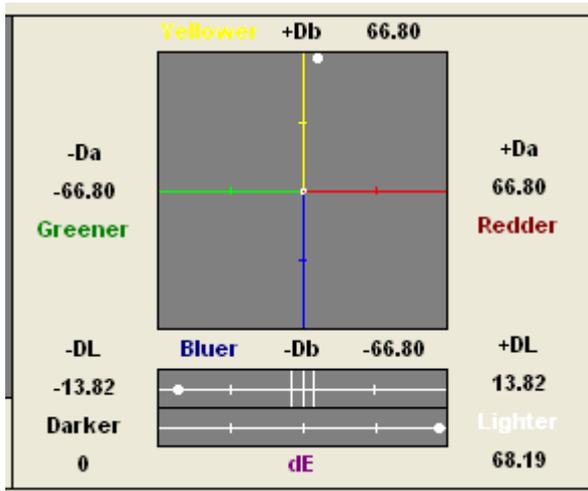
Image at time interval



TSC Stabilized Cu nano (Fresh)



TSC Stabilized Cu nano (After 72 hrs)



TSC Stabilized Cu nano (After 4 weeks)

FIGURE 7.8

Colour difference in TSC stabilized Cu nano colloidal solution on storage in atmospheric condition

After 4 weeks, the colour is changed to redder side. Cu nano particles get surrounded by the citrate ions released from tri-sodium citrate and each sphere of Cu the nano particles surrounded by the citrate anions repelled each other and prevented further aggregation of the nano particle.

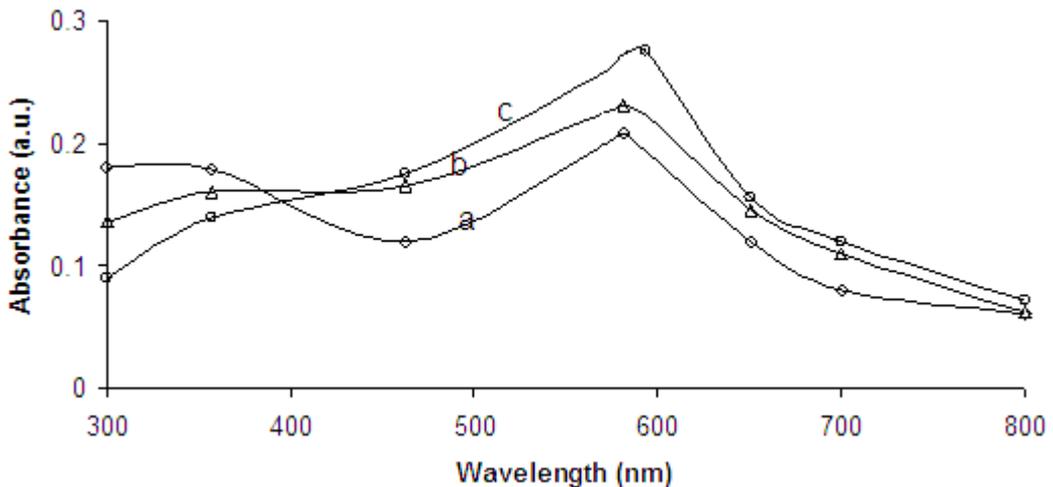


FIGURE 7.9

UV-VIS spectra of TSC capped Cu nano colloids of various time intervals [Time after synthesis: (a) 12 hours, (b) 18 hours and (c) 24 hours] [20]

The stability of the TSC capped copper nano colloid was then assessed by examining the absorbance spectra of the solution for finer time intervals viz. 12 hours, 18 hours and 24 hours. From figure 7.9 (a & b) it is found that there was no change in λ_{max} value for storing the solution for 12 hours and 18 hours

but the colour intensity was increased after 18 hours as seen from the increase in absorbance value. As the particles gain size, the absorption peak usually shifts towards redder side as we find in Figure 7.9 c. Increase in absorption indicates that the quantity of Cu nanoparticles increased. The stable position of absorbance peak in Figure 7.9 a and 7.9 b indicate that new particles do not aggregate. During the initial trial experiments when Cu nanoparticles were synthesized without the addition of stabilizing agent, the yellow colour of the solution was persisted for few hours only in atmospheric condition. Further work, therefore, confined to TSC stabilized nano colloids.

Characterizations of TSC stabilized copper nanoparticles

Figure 7.10 (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 inset photographs of the absorbance curves that how a blue green solution of copper sulphate gradually turned to yellow indicating the formation of Cu nanoparticles.

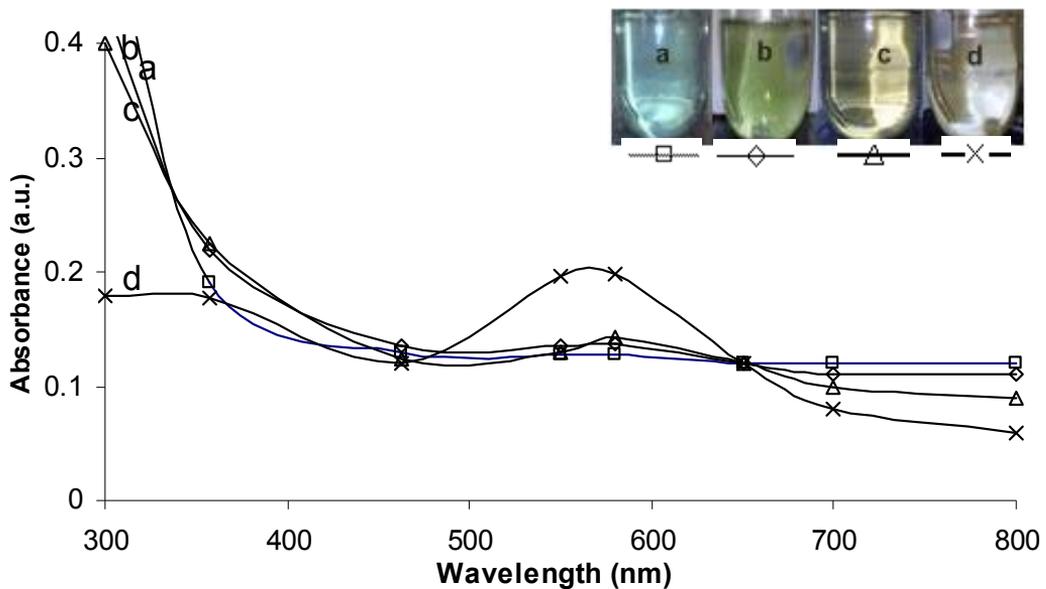


FIGURE 7.10

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) Stage 4: TSC stabilized Cu nano colloids. [20]

The shifting of blues-green colour of CuSO_4 solution to intense yellow 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 7.10 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 [21]. 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 as reported by Henglein [22]. The wavelength of oscillation 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 [19].

The particle size and size distribution of the prepared and stabilized Cu colloid were analyzed on Malvern instrument. Figure 7.11 (a) shows the intensity size distribution of Cu nano particles dispersed in water.

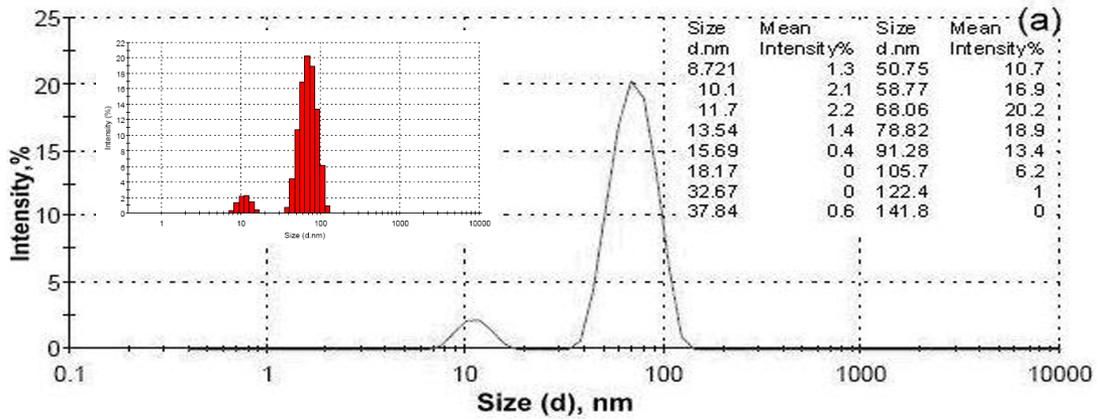


FIGURE 7.11 Particles Size and its distribution for synthesized and TSC stabilized Cu nano colloids; (a) by Intensity

The first peak at around 10 nm was arised from dispersion; the peak position at around 70 nm arises from stabilized Cu nano particles. Elemental analysis of gold coated Cu nano particles were performed on oxford Inca softwar using Scanning Electron Microscope (SEM). Figure 7.12 (a) shows the image analysis results of Cu nano particles. The elemental analysis results presented in Figure 7.12 (b) confirms the presence of copper particles. Peaks for carbon, gold, sodium also observed which got contaminated during the preparation of sample for elemental analysis.

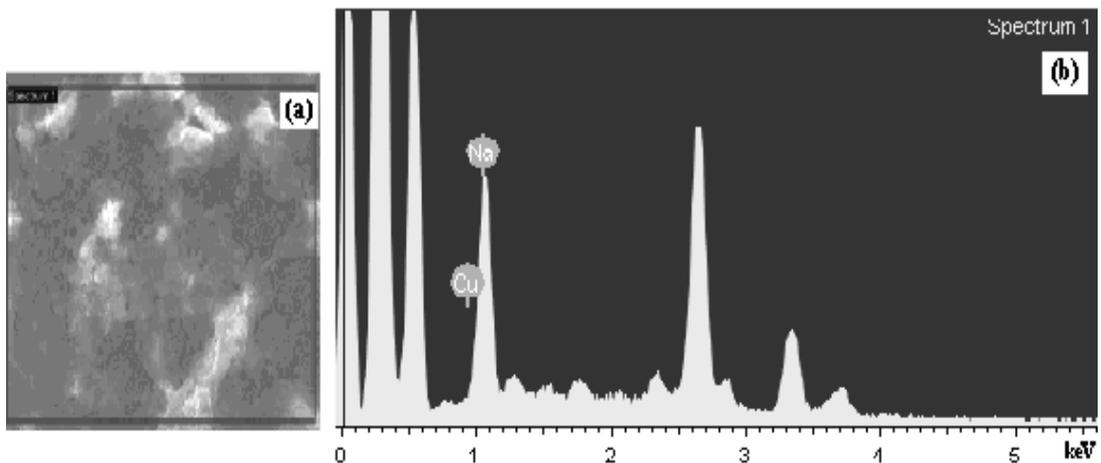
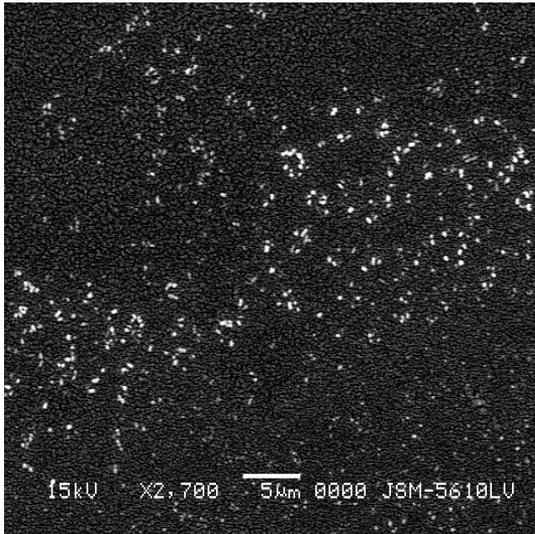
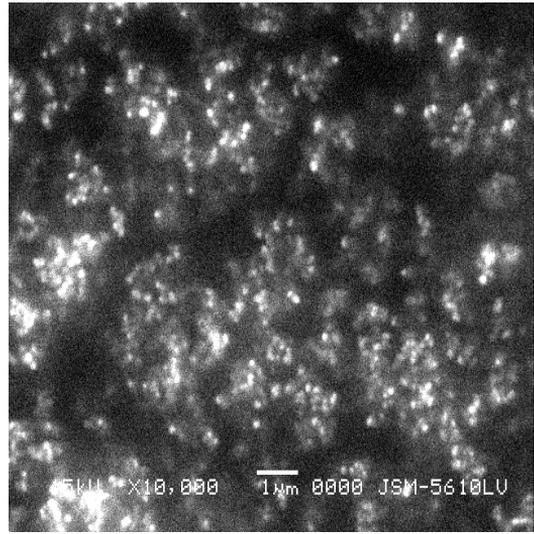


FIGURE 7.12 (a) SEM image of selected area of gold coated Cu nano particles (b) Elemental analysis of the synthesized particles using Inca software

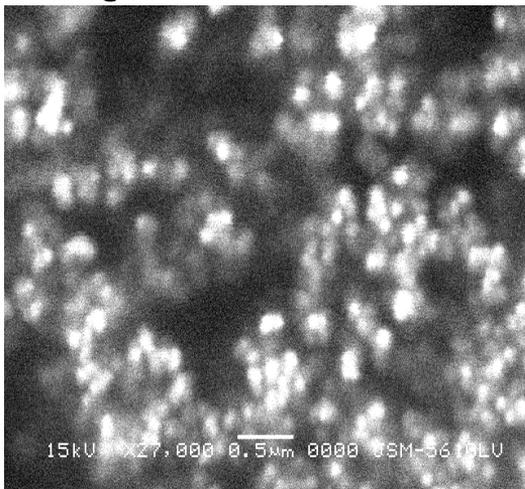
Figure 7.13 shows the scanning electron micrographs of stabilized Cu nano particles deposited on carbon coated aluminum sheet. From the images observed at 2700X, 10000X and 27000X it seems that the synthesized Cu nano particles were roughly spherical in shape.



Cu Nano@ 2700 X



Cu Nano@ 10000 X



Cu Nano@ 27000 X

FIGURE 7.13

Scanning Electron Microscope (SEM) images of copper nano particles

The average size as seen from the scale of the photograph is about 60-100 nm which is also in agreement with the size distribution found using particle size analyzer

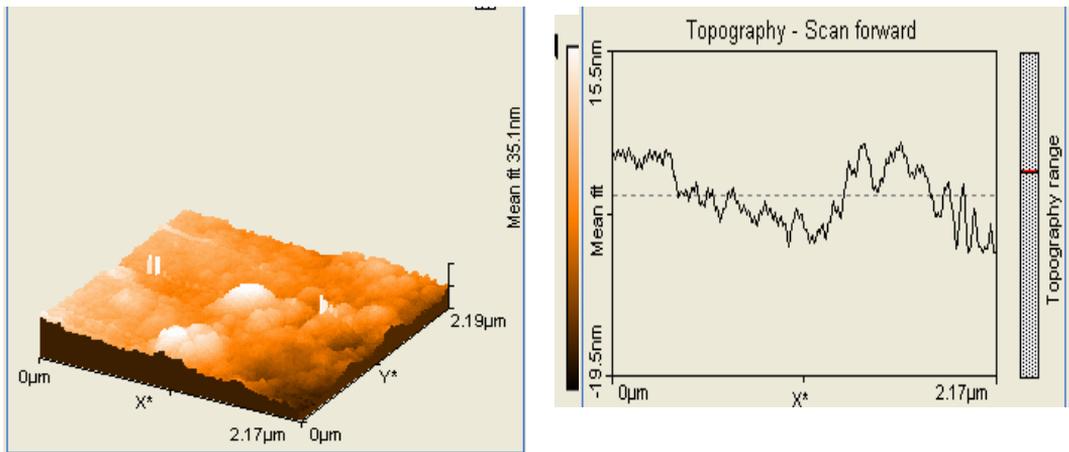


FIGURE 7.14

Atomic Force Microscopic image and topography of synthesized and TSC stabilized Cu nano colloids [5]

The copper nano particles were deposited on glass plate for observation under atomic force microscopy (AFM). The size of nano Cu particles as seen from the scale on the AFM image (Figure 7.14) and topography lies below 100 nm, which also supports the results, obtained using particle size analyzer and SEM.

In situ formation and stabilization of copper nanoparticles on polyester fabric

As discussed earlier in this chapter , the in-situ synthesis and stabilization of the copper nano particles were done by impregnating polyester fabric first with chilled sodium borohydride followed by padding with copper sulphate solution and finally in-situ synthesis of nano particles and their locking in the fibre structure were done by curing at high temperature 180 °C for 60 seconds. Figure 7.15 shows the image and CCM colour coordinate of the fabric loaded with in-situ synthesized copper nano particles. Scanning electron microphotographs of the untreated and treated polyester are shown in figure 7.15. The surface deposited nano particles are seen in the SEM image of the treated polyester fabric.

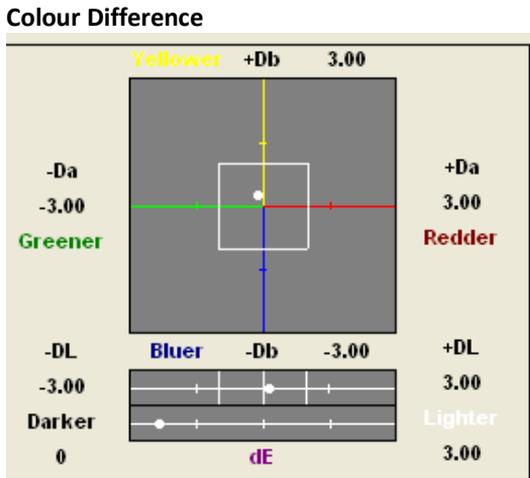


Image
Photograph of fabric loaded with In-situ synthesized Cu nano particles

FIGURE 7.15
Colour difference values of copper nano loaded polyester fabric

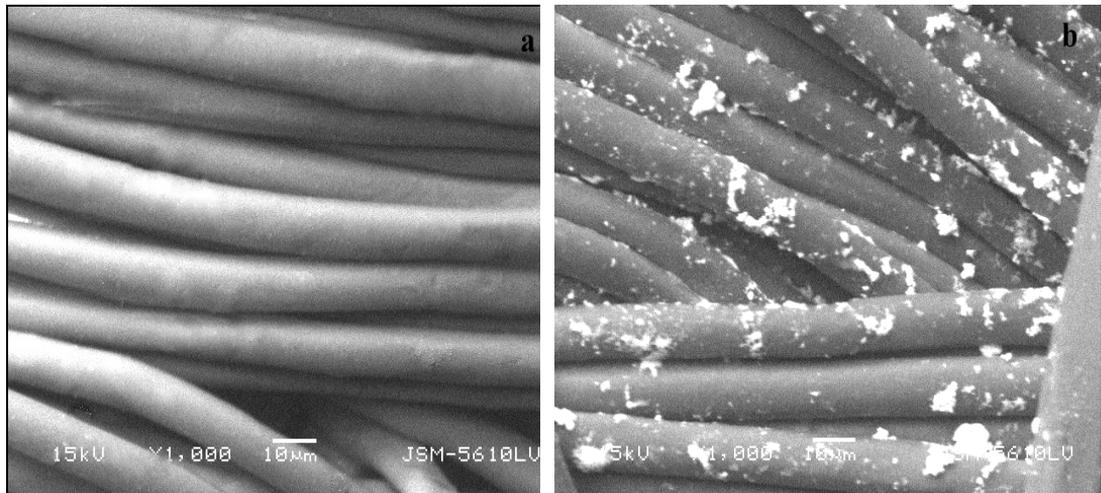


FIGURE 7.16
Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized copper nano particles on polyester fabric

Both the treated and untreated polyester were analyzed on X- ray fluorescence spectroscopy for the detection and measurement of elemental copper respectively. The amount of copper found in the treated polyester was about 0.16 μg against nil for untreated one.

TABLE 7.3
Amount of copper detected on 78.5 mm² polyester with XRF

Structure	Amount of copper , μg
PET	Nil
Cu/PET fabric	0.16

Synthesis of colloidal silver nanoparticles

Silver nano colloidal particles were synthesized from silver salt by chemical reduction technique. The reduction of silver salt to silver nano particles was observed at different stages by computer colour matching system. The change in the colour of silver salt solution with the addition of reducing agent is shown in Figure 7.17. The progressive changes in the colour of the solution during the synthesis of silver nano particles were captured using computer colour matching system.



FIGURE 7.17

Progressive colour change of silver sulphate solution during the preparation of silver nano particles

Figure 7.17 shows (i.e. stage 1-8) the gradual change in colour of silver salt during synthesis. Stage 1 presents the colour of silver sulphate solution before the addition of reducing agent. As the reaction proceeds i.e. with gradual addition of reducing agent, the colour of silver salt solution gradually changed to yellow (stage 7). After the addition of stabilizer TSC, colour of the solution was turned orange (stage 8) [15].

Change in colour of the synthesized silver nano colloid stored in atmospheric condition without stabilizing agent

After synthesis, silver nano colloidal particles (in absence of capping agent) were analyzed for its change in colour using CCM system at different time intervals i.e. (i) just after synthesis, (ii) after storing for 48 hrs, and (iii) after storing for 72 hrs in atmospheric condition. From the results presented in Figure 7.19, it can be seen that even after storing for 72 hrs in atmospheric condition the colour of solution shifted towards red. But after 4 week of storing time the colour of the colloidal solution, changed to black.

Colour Difference

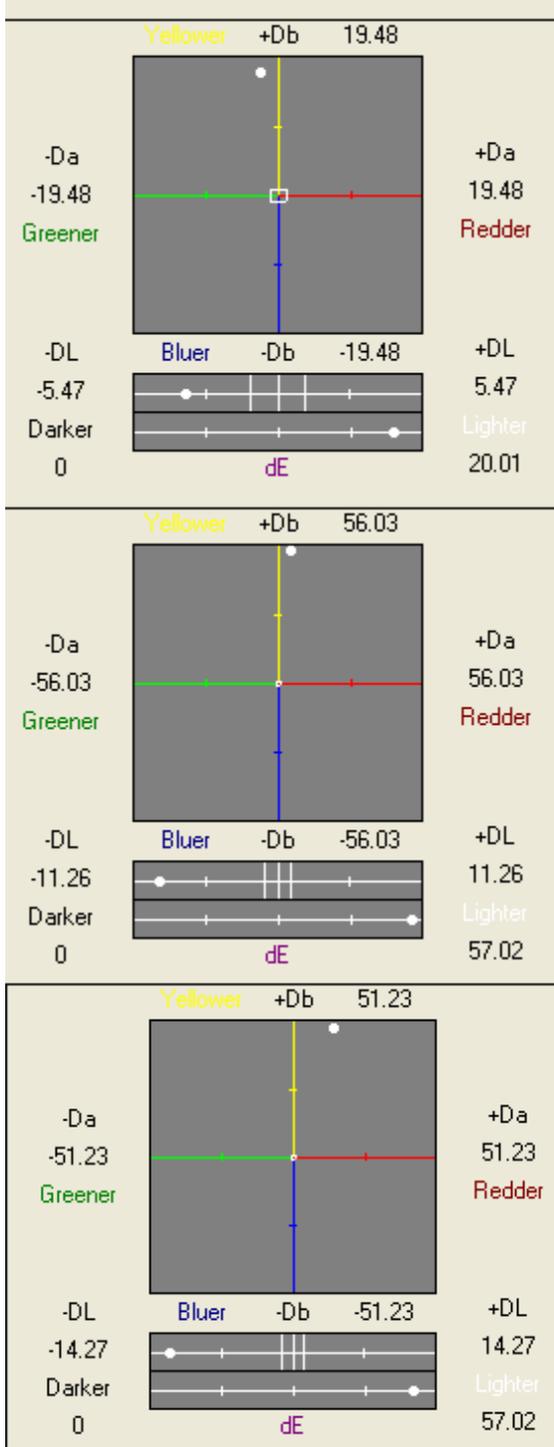


Image of colloidal solution



Ag nano (Freshly prepared)



Ag nano (after storing for 48 hrs)



Ag nano (after storing for 72 hrs)

FIGURE 7.18

Colour difference in Ag nano colloidal solution on storage in atmospheric condition (in absence of capping agent)

Stability of the TSC capped silver nano colloids in atmospheric condition

For examining the stability of the TSC capped nano silver colloid stored in atmospheric condition, the absorption spectra of the colloid were recorded measured at different time intervals viz. after 1 h, 2 weeks and 4 weeks which are shown in Figure 7.19. The UV-VIS spectrums recorded after different time intervals are shown in Figure 7.19 (a, b and c).

It is found that the stabilized silver nano colloidal solution gives an absorbance peak at 445 nm due to plasmon resonance of the nanoparticles. Similar observation was also reported by Šileikaitė et al [15]. The plasmon peak and the full-width of half-maximum (fwhm) depend on the extent of colloid aggregation.[8]

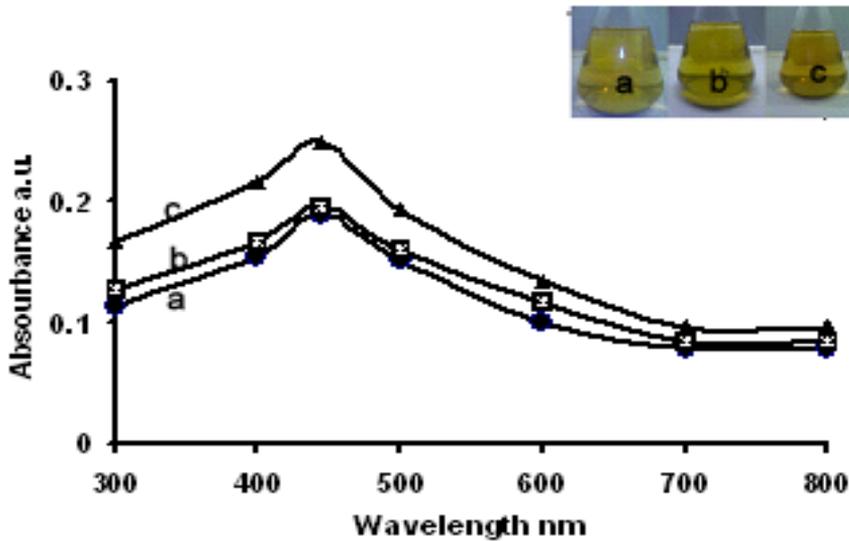


FIGURE 7.19

UV-VIS spectra of Ag colloids [time after synthesis: (a) 1 h, (b) 2 weeks and (c) 4 weeks] [3]

There was no change in the peak position found even after storing for 4 weeks. The inset photograph (Figure. 7.19) shows that there is no reasonable change in the colour of the colloidal solutions except little darkening of colour when stored for 4 weeks. The stable position of the absorbance peak (λ_{\max}) indicates that the particles do not aggregate. The increase in absorbance value after storing for 4 weeks is indicative of increase in concentration of the nanoparticles through the generation of new particles.

Characterizations of TSC stabilized colloidal silver nanoparticles

Nano sized Ag particles in colloidal form prepared by chemical reduction technique were characterized for their size, shape and elemental analysis. The particle size and size distribution of stabilized nano Ag colloid were analyzed on Malvern instrument. Figure 7.20 shows the intensity size distribution of Ag nanoparticles dispersed in water. The first peak at around 110 nm arises from the dispersion.

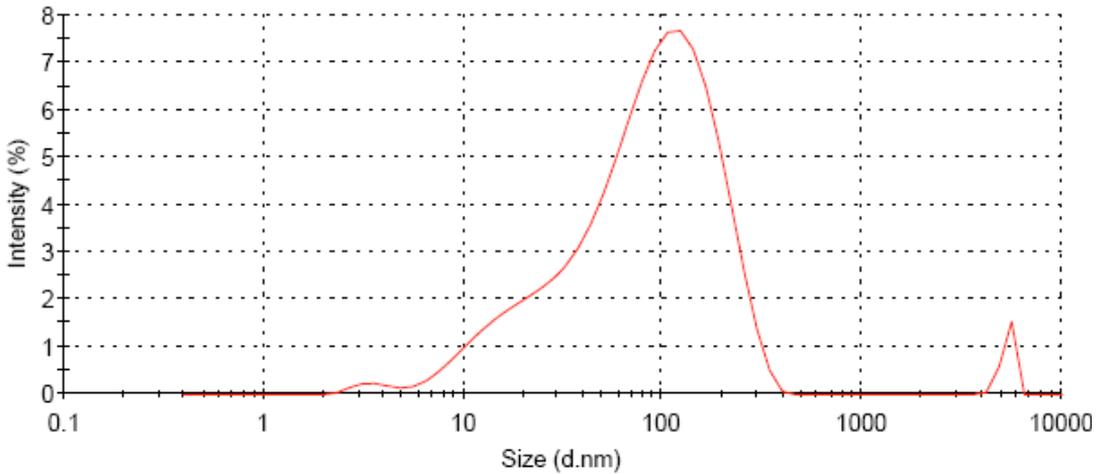


FIGURE 7.20
Particle size distribution of stabilized Ag nanoparticles by intensity

The peak positioned at 4 microns was arised from the stabilized Ag nanoparticles. The presence of the second peak has resulted in the Z-average diameter for this sample increasing to 62.06 nm. It is also evident from the particle size analysis that most of the nano particles are in the range of 60 nm to 120 nm.

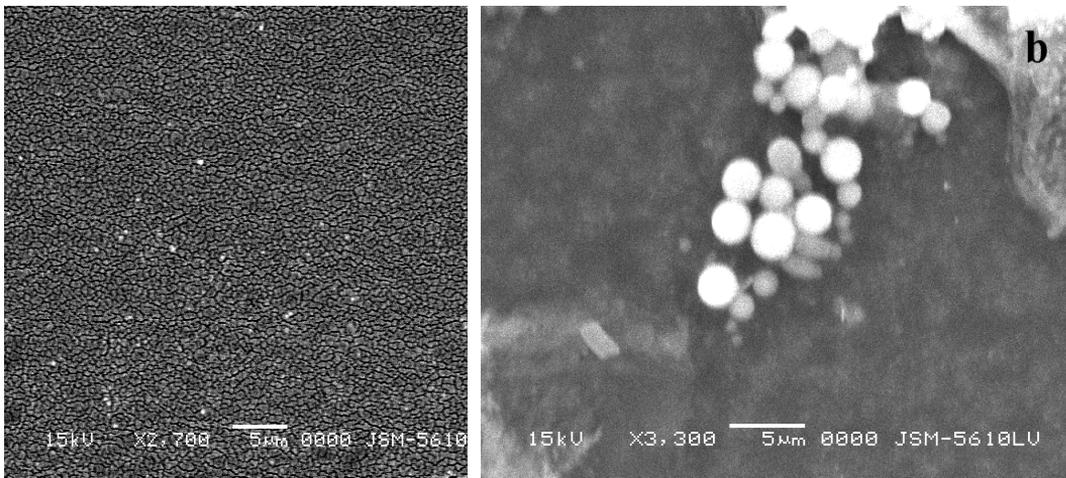


FIGURE 7.21
Scanning electron microphotographs of silver nanoparticles (a) deposited on carbon coated aluminum sheet and (b) coated with gold and deposited on carbon coated aluminum sheet [3]

Figure 7.21a shows the scanning electron microphotographs of stabilized Ag nanoparticles deposited on carbon coated aluminium sheet. The average size as seen from the scale of the photograph is approximately below 90-100 nm which also supports the size obtained using particle size analyzer. Figure 7.21b represents the microphotographs of the gold coated Ag nanoparticles. It can be seen from

the figure that the shape of the gold coated particles is spherical and the size of nanoparticles is increased by 500 – 800 nm due to the gold coating.

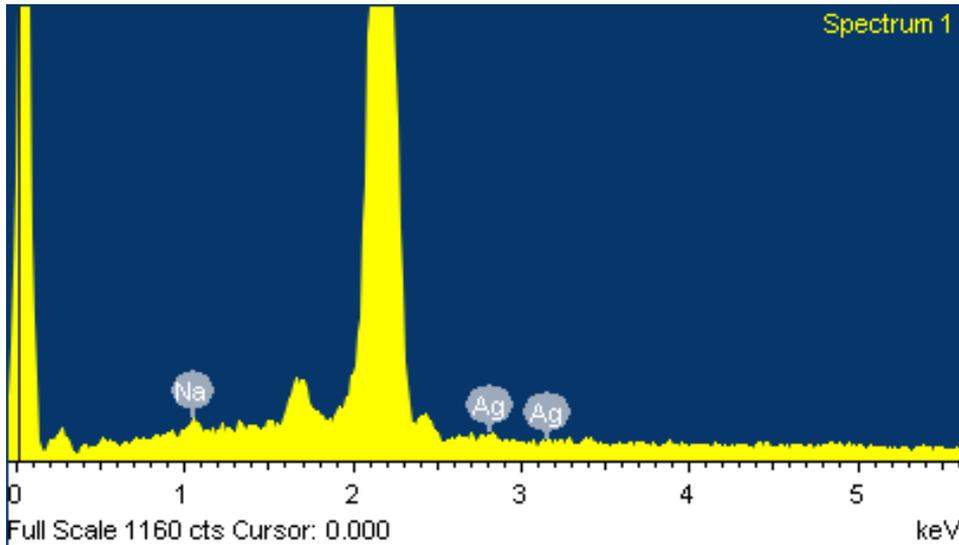


FIGURE 7.22

Elemental analysis result of silver nanoparticles deposited on carbon coated aluminum sheet and further coated with gold

Elemental analysis of gold coated nanoparticles was performed on the scanning electron microscope using special software. The result observed in this test is shown in Figure 7.22. Presence of silver is confirmed by the elemental analysis curve. The peaks for carbon, gold and sodium have also been observed.

In situ formation and stabilization of silver nanoparticles on polyester fabric

The in-situ synthesis and stabilization of the silver nano particles were done by impregnating polyester fabric first with chilled sodium borohydride followed by padding with silver sulphate solution and finally in-situ synthesis of nano particles and their locking in the fibre structure were done by curing at high temperature 180 °C for 60 seconds. Figure 7.23 shows the image and CCM colour coordinate of the fabric loaded with in-situ synthesized silver nano particles. It can be seen from the figure that the colour of polyester fabric after synthesis of silver nano by in-situ technique was turned to yellow. Scanning electron microphotographs of the untreated and treated polyester are shown in figure 7.24. The surface deposited nano particles are seen in the SEM image of the treated polyester fabric.

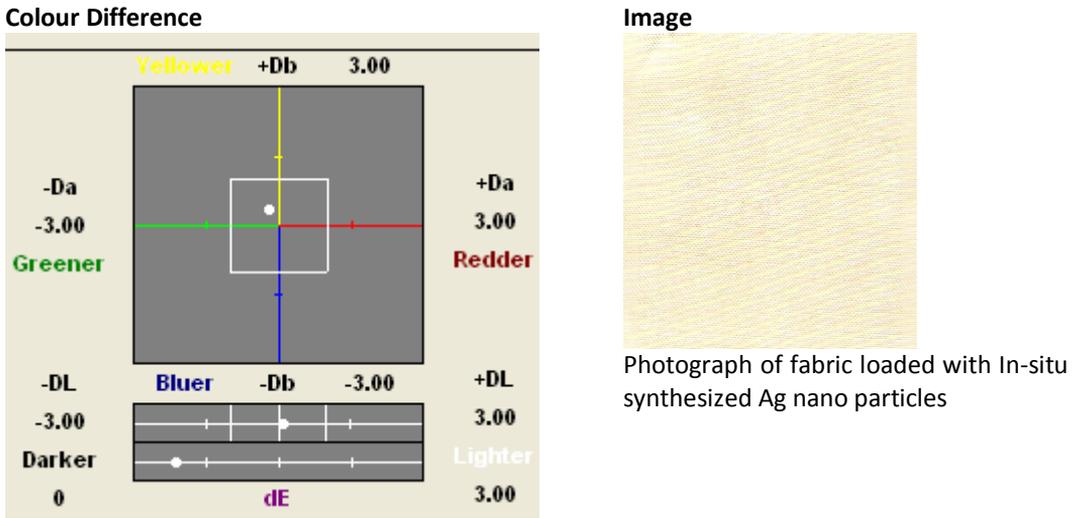


FIGURE 7.23
Colour difference values of Ag nano loaded polyester fabric

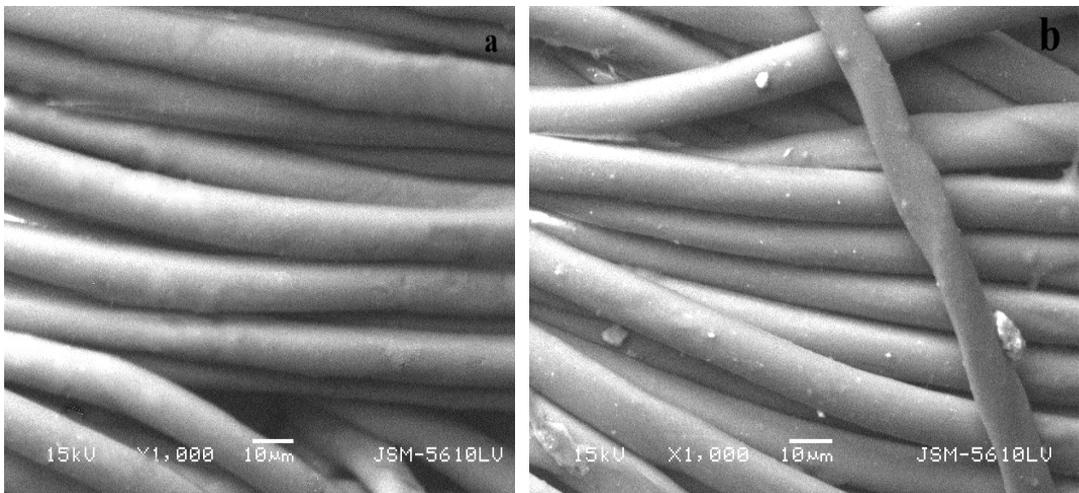


FIGURE 7.24
Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized silver nano particles on polyester fabric

The amount of silver as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm². From Table 7.4 it can be seen that the amount of silver found in the treated polyester was about 0.103 µg against nil for untreated one.

TABLE 7.4

Amount of silver detected on 78.5 mm² polyester with XRF

Structure	Amount of silver , μg
PET	Nil
Ag/PET fabric	0.103

Synthesis of colloidal zinc nanoparticles

Zinc nano colloidal particles were synthesized from zinc salt by chemical reduction technique [4]. The absorption spectrum of the prepared colloidal solution dispersed in water is shown in Figure 7.25. It is found that the solution after synthesis gives an absorbance peak at 370 nm. Similar observation at ~375 nm was also reported by Zhang, et al (2002) [23]. Figure 7.25(a, b and c) represent the absorption spectra of different stages during the formation of zinc nanoparticle colloid from zinc salt solution. It is seen from the absorbance curves that how a clear solution of zinc salt gradually turned to milky white indicating the formation of zinc nanoparticles.

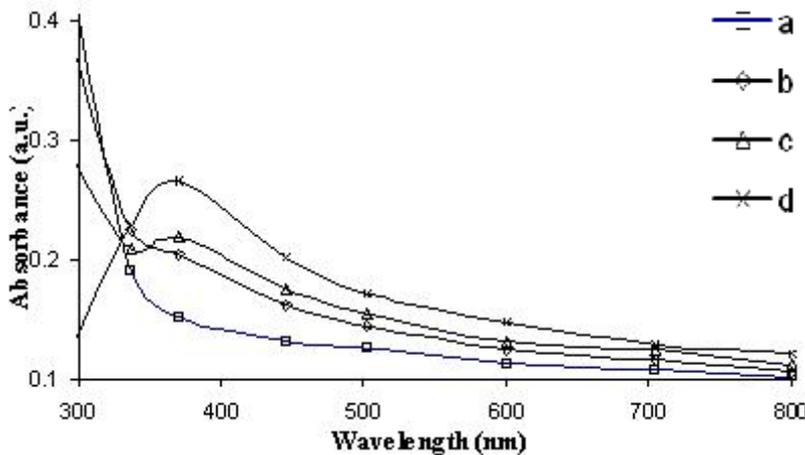


FIGURE 7.25

The UV-VIS spectrums of Zn nano colloids at different stages of synthesis [(a) Stage 1: Zn salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Zn nano colloids and (d) Stage 4: TSC stabilized Zn nano colloids.] [4]

Stability of the synthesized zinc nano colloid stored in atmospheric condition without stabilizing agent

After synthesis, zinc nano colloidal particles were stored in atmospheric condition for different time intervals, i.e. (i) for 48 hrs and (ii) storing for 72 hrs in atmospheric condition. The colour difference evaluated by CCM and corresponding photographs of the solution given in Figure 7.26, it can be seen that after storing for 72 hrs in atmospheric condition the intensity of the solution was slightly changed. But after that the bigger particles settled down at bottom of the flask and the solution become clear.

Colour Difference

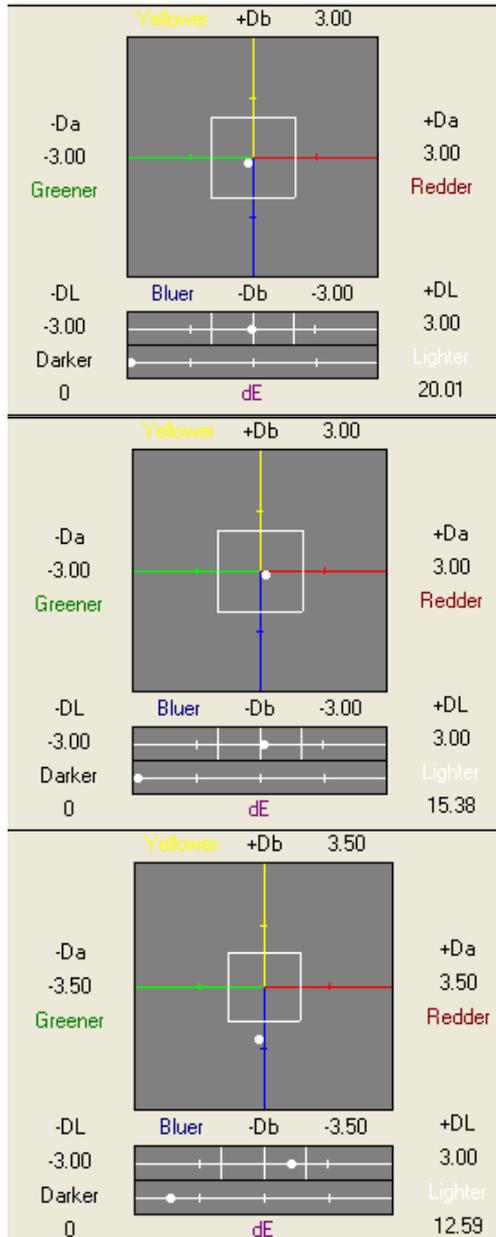


Image at time interval



Zn nano (Freshly prepared)



Zn nano (after storing for 48 hrs)



Zn nano (after storing for 72 hrs)

FIGURE 7.26

Colour difference in Zn nano colloidal solution on storage in atmospheric condition without capping

Characterizations of TSC stabilized colloidal zinc nanoparticles

Zinc particles were prepared by reduction of zinc salt and stabilized with citrate anions. The nano Zn particles in the solution were characterized for their size, shape and elemental analyses

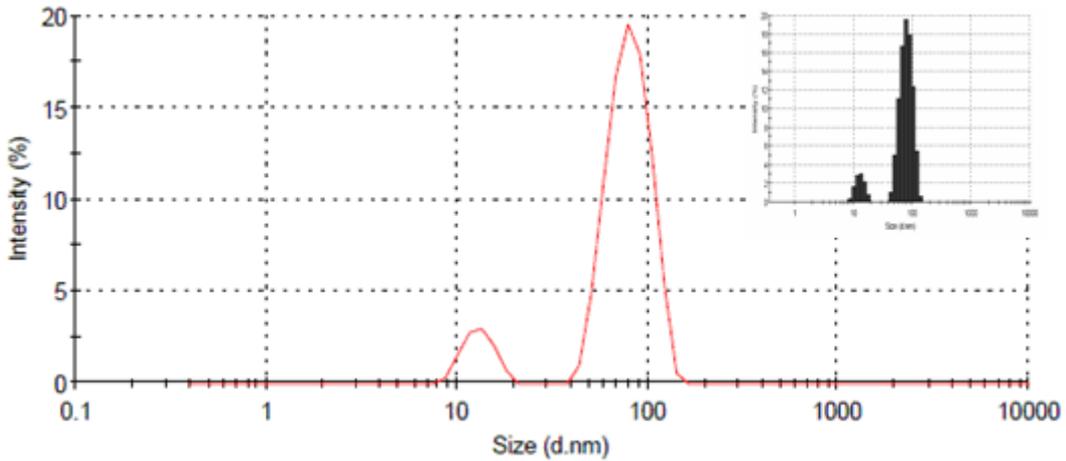


FIGURE 7.27
Particle size distributions of stabilized Zn nanoparticles by intensity [4]

The particle size and size distribution of the prepared and stabilized Zn colloid were analyzed on Malvern instrument. Figure 7.27 shows the intensity size distribution of Zn nano-particles dispersed in water. The first peaks at around 15 nm arise from dispersion; this peak represents nano particles of size 13.14 nm diameter. The presence of second peak has resulted in the average diameter of 81.62 nm. Figure 7.29 shows the scanning electron micrographs of Zn nano-particles. The average size as seen from the scale of the photograph is below 100 nm which is in agreement with the size distribution found using particle size analyzer.

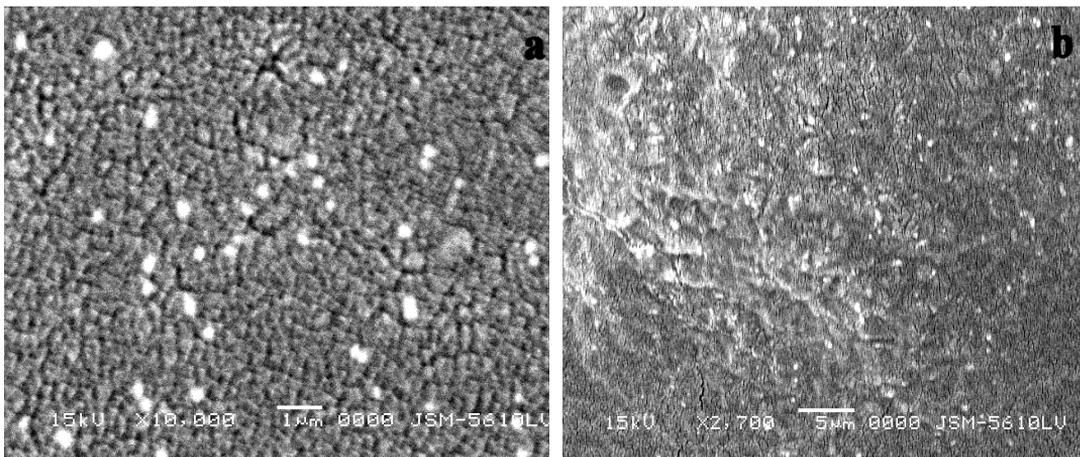


FIGURE 7.28
Scanning electron microphotographs of silver nanoparticles (a) deposited on carbon coated aluminum sheet and (b) coated with gold and deposited on carbon coated aluminum sheet [4]

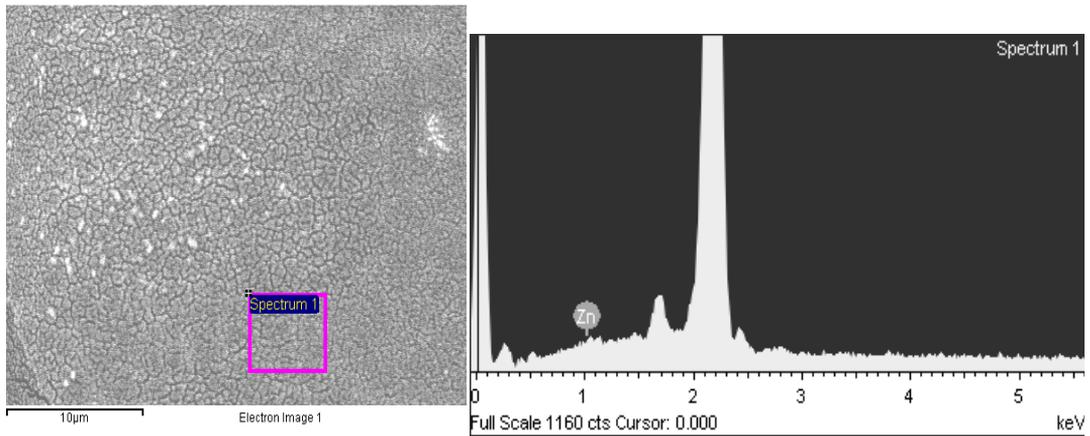


FIGURE 7.29

SEM micrograph and EDX spectrum of selected area of nano-particles deposited carbon coated aluminium sheet and further coated with gold [4]

Figure 7.29 represents the elemental analysis result which confirms the presence of zinc. Peaks for carbon, gold, sodium also were observed which are used for the preparation of sample for elemental analysis.

In situ formation and stabilization of zinc nanoparticles on polyester fabric

As shown in the Figure 7.2 an experimental set up was designed for the continuous synthesis and simultaneous application of Zn nano particles to polyester fabric. The SEM microphotograph of treated polyester fabric (Figure 7.30) confirms the uniform deposition of nano particles on the surface of the fabric. The SEM image also confirms that the average size of the synthesized Zn nanoparticles is remaining below 100 nm and the shape of the particle is spherical.

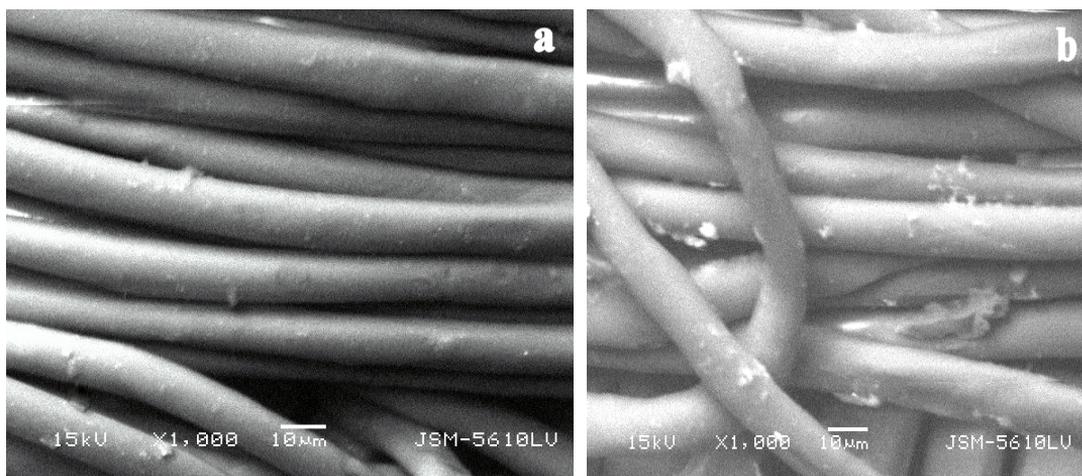


FIGURE 7.30

Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized zinc nanoparticles on polyester fabric

The amount of zinc as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan).

Conclusions

In this study, nanoscaled copper, silver and zinc metal colloidal solution (10-100 nm) were synthesized in water by borohydride reduction method under atmospheric conditions.

In first phase of the research, nano copper colloids were prepared, by reducing Cu^{+2} ions using chemical bath deposition technique. The absorbance spectrum of the solution was observed 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. Similar trend was observed in AFM study. The stability of the particles was improved by the introduction of citrate anions in the colloidal system. In this system the particles were found to be quite stable even up to 4 weeks. These particles were observed by SEM technique. It reveals that with the adopted method of synthesis and stabilization it is possible to keep the prepared copper nano below 100nm size, a qualifying limit to be called as nanoparticles.

The formation of silver nanoparticles was confirmed by uv-vis absorption and elemental analysis results. Study on ageing of synthesized silver nano was carried out by uv-vis measurements confirmed that the size of the nanoparticles in colloid did not changed, but with time the concentration slowly increased within few weeks. The z-average size of the synthesized silver nano particle was found to be 62.06 nm. The SEM images have indicated that silver nanoparticles produced were of spherical in shape.

It is found that the zinc solution after synthesis gives an absorbance peak at 370 nm. The scanning electron micrographs of Zn nano-particles, the average size as seen from the scale of the photograph is below 100 nm which is in agreement with the size distribution found using particle size analyzer. The most significant result of the study is that the new in-situ method resulted in most easy and economical, which could not be attained by chemical reduction method.

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