Paper ID: MS-18

Preparation and Properties of Chemically Reduced Cu and Ag Nanoparticles

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Abstract

Metallic nanoparticles like copper (Cu) and silver (Ag) were prepared by simple chemical reduction method. The synthesis of Cu nanoparticles was performed by the reduction of copper sulfate ($CuSO_4$) with hydrazine hydrate in aqueous solution under atmospheric air in the presence of sodium dodecyl sulfate (SDS) as capping agent. Likewise, Ag nanoparticles were reduced by $NaBH_4$ from the solution of $AgNO_3$ in water. The synthesized nanoparticles were characterized by UV-Visible absorption spectra, FT-IR and optical microscopic images.

Keywords: *nanoparticles, chemical reduction, hydrazine hydrate, SDS, UV-visible spectra.*

1. Introduction

Nanotechnology has become one of the most interesting areas of scientific research in recent years, particularly in the area of material research, including the synthesis, characterization and application of nanometer-sized metals, oxides, semiconductors and ceramics [1]. Nanoparticles (NPs) exhibit electronic and optical properties different from those displayed by their bulk-material counterparts. These properties can further be tuned by altering the dimensions and their mutual interactions [2-5]. Gold, silver and copper stable dispersions of nanoparticles are useful in areas such as microbiology, surface-enhanced Raman scattering (SERS) detection, photography, catalysis, biological labeling, photonics and optoelectronics [3]. The antifouling properties of copper and silver are well known and their effectiveness at reducing the growth of various microorganisms has been reported [6-8].

Nanoparticles are small and not thermodynamically stable for crystal growth. Therefore, the nanoparticles must be protected during the reaction either by adding surface-protecting agents such as organic ligands and inorganic capping materials or by placing in inert environment such as inorganic matrix and polymers.

A variety of preparation routes have been reported for the preparation of metallic nanoparticles [9, 10]; notable examples include, metal vapour deposition, electrochemical reduction, radiolysis, thermal decomposition, ultrasonic irradiation, mechanical attrition and chemical reduction. Among these methods, the solution method is found to be simple and most versatile for metal nanoparticles [11]. In this paper, we report the synthesis and properties of SDS capped copper and silver nanoparticles by chemical reduction method.

2. Experimental details

2.1. Materials

The chemical materials of Cupper Sulfate (>99.98% $CuSO_4$), Silver Nitrate (>99.5% $AgNO_3$), Sodium Borohydride ($NaBH_4$) and Hydrazine Hydrate were purchased from Merck (Germany) and NaOH & SDS were from Merck (India). All of the chemicals were analytical grade and used as purchased without further purification. Redistilled water was used to prepare all of the solutions.

2.1. Preparation of Cu and Ag nanoparticles

The copper NPs were prepared in aqueous phase by chemical reduction of $CuSO_4$ with hydrazine hydrate in the presence of SDS as capping agent. NaOH was used to adjust the p^H of the solution and accelerate the reduction reaction in water. In a typical experiment, 1ml of 0.5M NaOH was added with 100 ml of 10 mM $CuSO_4$ solution and stir for a time period of 10 minutes. 1 ml of 0.1 M SDS solution was then added drop-wise to the solution under a continuous stirring. After 10 minutes 2 ml of 80% hydrazine hydrate was added drop-wise to the above solution under constant stirring. The color of the reaction solution changed to reddish black on complete addition of reducing agent indicating the formation of copper nanoparticles.

On the other hand, Ag NPs were prepared according to K.C. Song et al.[12]. Here Ag nanoparticles were synthesized from $AgNO_3$ precursor by using $NaBH_4$ and SDS as reducing agent and stabilizer, respectively. $AgNO_3$ solution was prepared by dissolving the required amount of $AgNO_3$ in distilled water. Separately, the $NaBH_4$ solution was prepared by dissolving $NaBH_4$ and SDS in 45 ml distilled water for a period of 20 minutes together. After that 5 ml of $AgNO_3$ solution added drop-wise into the $NaBH_4$ solution with SDS slowly. After all solutions were added, the mixed solutions were stirred for a half an hour more.

2.3. Characterization

The surface plasmon absorption spectra of Cu and Ag nanoparticles were measured with a SHIMADZU UV-1650PC UV-visible spectrophotometer. During the experiment, the colloidal sample was filled in clean quartz cell for measurement. The scanning region was from 300 to 700 nm. To investigate the morphology and shape of the nanoparticles high resolution optical microscope (Olympus-IX-71) was used. Fourier Transform Infrared (FT-IR) spectroscopic measurements were done using Perkin Elmer 100E spectrophotometer.

3. Results and discussion

3.1. UV-visible Spectroscopy

UV–visible absorption spectra and color of copper nanoparticles are shown in Fig. 1. From the figure it is reveal that chemically synthesized copper nanoparticles solution appears as reddish black in color and has the characteristic absorption peak at around 575nm which is well reported signature of copper nanoparticles formation [13-15]. The strong surface-plasmon band may depend on the individual particle property including sizes, shapes, solvents and reducing agents employed. The strong surface-plasmon absorption band observed at 575nm may due to the formation of non-oxidized copper nanoparticles. The broadness of the absorption band (Fig. 1) probably arises from the wide size distribution of copper nanoparticles.

Figure 2 shows the UV-visible absorption spectra of Ag nanoparticles prepared with different initial $AgNO_3$ concentrations. All the other conditions were constant as 0.01M $NaBH_4$ and 0.01M SDS. The color of the solutions depends on the concentrations of added $AgNO_3$ solutions. With increasing the initial concentration, the color of the solution changed from light yellow to brown. A minor blue shift observed at the absorption peak with increasing the initial $AgNO_3$ concentrations. This may be due to formation of smaller size nanoparticles with higher $AgNO_3$ concentrations. The absorption peak at around 405nm in Fig. 2 is attributed to the surface plasmon excitation of silver nanoparticles, indicating the formation of silver nanoparticles [9,12,16]. From this figure, it also observed that the peak intensity of the samples increases with increasing $AgNO_3$ concentrations which could be attributed to the generation of highly dense and smaller particles.

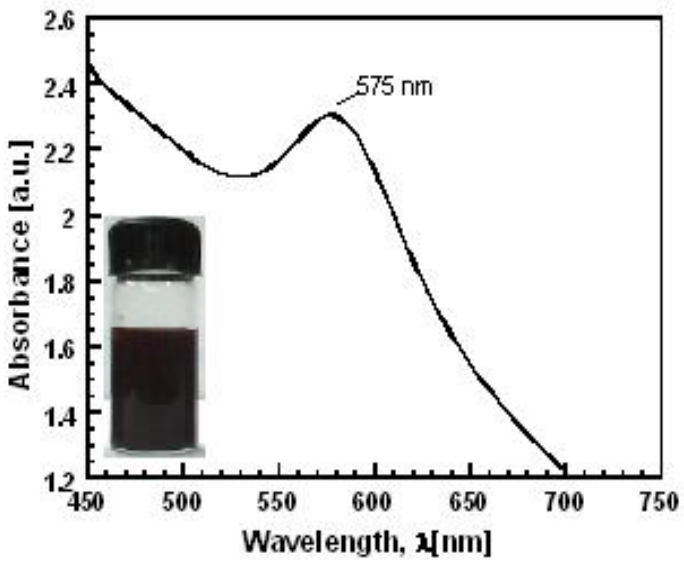


Fig. 1. UV-visible absorption spectrum and color of copper nanoparticles

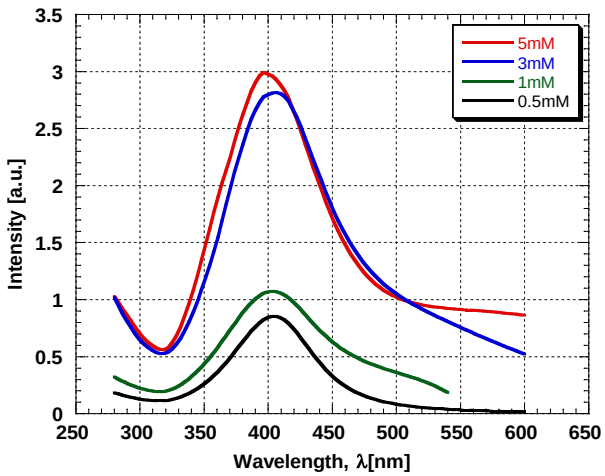
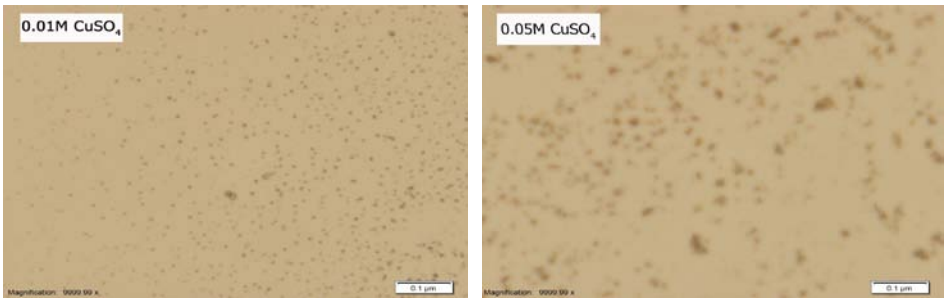
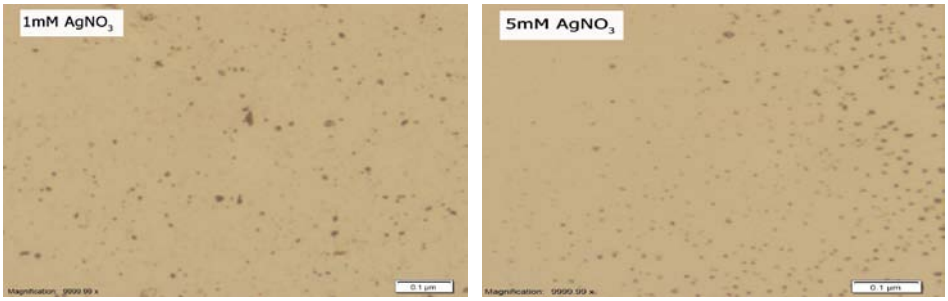


Fig. 2. UV-visible absorption spectra of Ag nanoparticles with varying initial $AgNO_3$ concentrations



(a)



(b)

Fig. 3. Microscopic images of (a) Cu NPs having initial precursor concentration of 0.01M and 0.05M, and (b) Ag NPs with initial precursor concentration of 1mM and 5mM.

3.2. Optical Microscopy

Copper and silver nanoparticles were characterized by high resolution advanced optical microscope to determine the morphology and size of the prepared nanoparticles. Fig. 3 shows the microscopic images of Cu and Ag nanoparticles. From this figure it is seen that the size of the nanoparticles changes with concentrations and the average sizes of the particles are less than 40nm with spherical structure.

3.3. Study of FT-IR

To examine the interaction between the SDS and copper nanoparticles, FT-IR spectra were recorded for SDS alone and SDS capped copper nanoparticles respectively. FT-IR spectrometry is useful for understanding the role of the organic molecules in this study. Fig. 4 shows the IR spectra of pure SDS and the copper nanoparticles coated with SDS in the range of 400–4000cm^{-1}. For pure SDS (Fig. 4(a)), the peak at 590 cm^{-1} due to the O-H out-of-plane bending and the peaks in the range of 610–1000cm−1 are attributed to the C–H bending vibration. The two absorption peaks that appear at 1081.23 and 1223.61cm^{-1} are due to the SO_3 stretching vibrations. The peaks at 1383.79 cm^{-1}, 1468.41 cm^{-1} and 1637.78 cm^{-1} are corresponding to CH_2 wagging, CH_3 and HOH bending vibrations, respectively. The CH_3 asymmetric (2957.03 cm^{-1}), the CH_2 asymmetric (2918.10 cm^{-1}), CH_3 symmetric (2873 cm^{-1}), CH_2 symmetric (2850.43 cm^{-1}) and OH (3461.96 cm^{-1}) stretching bands are also observed in the figure.

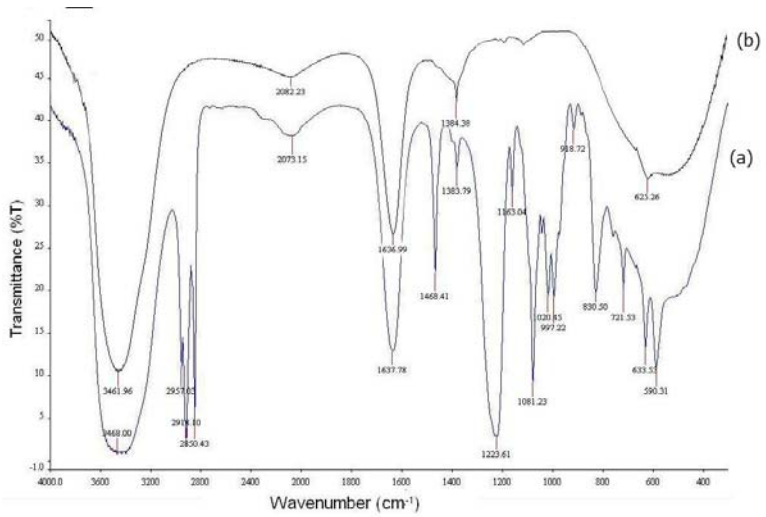


Fig. 4. The FT-IR spectra of (a) pure SDS and (b) SDS capped copper nanoparticles

Comparing Fig. 4(a) and (b), it observed that all the peaks in Fig. 4(b) are weaker, the stretching vibration of O–H bands at 3468.00 cm^{-1} and bending vibration of C–H band at 633.53 cm^{-1} in the spectrum of pure SDS is shifted to 3461.96 and 625.26 cm^{-1}, respectively, in the spectrum of the copper coated with surfactant. The HOH bending vibration band at 1637.78cm^{-1} and CH_2 wagging band at 1383.79 cm^{-1} are shifted slightly for coated copper nanoparticles. These peak shifts reveal that there exist an interaction between Cu nanoparticles and SDS. All other peaks that present in the spectrum of pure SDS are disappeared in the spectrum of the copper coated

with SDS. These dramatic differences indicate that a chemical bond could have been formed between SDS and Cu atoms on the surface of the copper nanoparticles.

4. Conclusions

Metallic nanoparticles were successfully synthesized by chemical reduction method. UV-visible absorption spectra of Cu and Ag nanoparticles give absorbance maxima at about 575 and 405nm, respectively. Sizes of the nanoparticles were changed with changing initial precursor concentrations. FT-IR study of Cu nanoparticles shows that a chemical bond could have formed between SDS and Cu atoms on the surface of the copper nanoparticles.

5. Acknowledgement

This work has been supported by the Faculty of Engineering, University of Rajshahi, Bangladesh.

6. References

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