Biogenic synthesis of Cu_2O nanoparticles using aqueous solutions of Arachishypogaealeaf extracts

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Abstract

Copper Oxide (Cu_2O) nanoparticles were rapidly synthesized by treating copper (II) ions with aArachishypogaea leaf extract. The reaction process was simple and convenient to handle, and was monitored using Ultraviolet-visible spectroscopy (UV-vis). The effect of Arachishypogaea leaf extract on the formation of Cu_2O nanoparticles was investigated using, Fourier-transform infrared spectroscopy (FTIR). The morphology and crystalline phase of the nanoparticles were determined from Scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectra. The results indicated that the carbohydrates, which have aldehyde groups, played a reducing and controlling role during the formation of Cu_2O nanoparticles in the solutions. The main conclusion is that green method to produce nanoparticles is a good alternative to the electrochemical methods.

Key words: Arachishypogaea L., Benedict's reagent, Cu_2O nanoparticles,

Introduction

Generally, Cu_2O nanostructures are either gained via oxidation of pure copper or obtained via reduction of Cu^{2+}. In the second method, a certain reducer is additionally introduced to the reaction system to obtain Cu_2O crystals. Upto now, a variety of approaches are available including catalytic reduction, seed mediated synthesis, micro emulsions, sonochemical preparation, alkoxide based preparation, microwave irradiation, precipitation-pyrolysis, thermal decomposition, thermal relaxation, liquid phase reduction, vacuum evaporation, sol-gel, flame spray, vapor-phase reaction, aqueous precipitation, template method, sacrificial anode technique, laser ablation in vacuum etc., [P. Jiang, et al., (2001), H.Zhang and Z. Cui, (2008), C.H. Kuo, et al., (2007), C.L. Carnes, et al., (2002), H.W. Wang, et al., (2002), Y. Yang, et al., (2004), S. Deki, et al., (1998), W. Wang, et al., (2002), H. Yanagimoto, et al., (2001), J. H. Gan, et al., (2004), R.K. Swarnkar, et al., (2009), L. Huang, et al., (2009)]. Various interesting copper oxide nanostructures such as cubes, cuboctahedra, octahedra, multipods, nanowires and hollow structures have been synthesized. They are mostly prepared by wet chemical reduction [C.H. Kuo and M.H. Huang, (2008)], electro deposition [S. Bijani, et al., (2007)], and solvothermal synthesis methods [Y. Xu, et al., (2007)].

Copper oxide is a perspective material with applications in magnetic storage media, catalysts, semiconductors, sensor, negative electrode material for lithium-ion batteries, template, metal-insulator-metal resistive switching memory, electrochromism, antibacterial activity, organic catalysis, CO oxidation, photocatalysis, photochemical evolution of H_2 from water, photocurrent generation, organic synthesis, photo catalytic degradation of organic pollutants etc [H. Xu, et al., (2006), L. Guan, et al., (2010), P. Poizot, et al., (2000), S. Jiao, et al., (2006), A. Chen, et al., (2008), O. Akhavan, et al., (2009), H. Pang, et al., (2009), J.F. Deng, et al., (19960, C. H. B. Ng and W.Y. Fan, (2006), M. Hara, ET AL., (1998), C.M. McShane and K.S. Choi, (2009), R. A. Altman, ET AL., (2007), Y. Tan, ET AL., (2007), B.D. Yuhas and P. Yang, (2009)]. The electrical properties of individual Cu_2O nanowires synthesized under hydrothermal conditions in the presence of poly (2, 5-dimethoxyanaline) have also been examined [P.E. de Jongh, D. Vanmaekelbergh and J.J. Kelly, (1999)]. A solar cell consisted of vertically oriented n-type ZnO nanowires, surrounded by a film constructed from p-type Cu_2O nanoparticles has recently been fabricated [B.D. Yuhas and P. Yang, (2009)].

Synthesis using bio-organisms, especially plants that secrete the functional molecules for the reaction, is compatible with the green chemistry principles. The bio-organism is (i) eco-friendly (ii) the reducing agent employed, and (iii) the capping agent in the reaction. The Arachishypogaealeavesposses biomolecules, such as polysaccharides, reducing sugars, amino acids and vitamins, which could be used as reductants to react with copper ions and as scaffolds to direct the formation of Cu_2O NPs in solution. To the best of our knowledge, the use of plant extracts at room temperature for the green synthesis of noble metal nanoparticles, such as Cu_2O NPs, has not been reported.

MATERIALS AND METHODS

Materials

All the chemicals including $CuSO_4.5H_2O$, sodium citrate, sodium carbonate, potassium thiocyanate, and potassium ferrocyanide were of analytical grade and were used as received from Merck Without further purification.

Preparation ofArachishypogaealeafextract

About 20g of freshly, taxonomically authenticated healthy leaves of Arachishypogaeawere collected, washed thoroughly with double distilled water, cut in to fine pieces and boiled with 100mL double distilled water in Erlenmeyer flask for 8-10 min. The extract was cooled to room temperature and filtered through Whattman filter paper (no.42).

Preparation of Benedict's reagent

It is prepared by dissolving 50g of sodium citrate, 18.75g of sodium carbonate and 31.25g of potassium thiocyanate in 159ml of hot distilled water. This is mixed with 25ml of an 8.38% (w/v) of $CuSO_4.5H_2O$ solution. 1.5ml of a 5% solution of potassium ferrocyanide is then added to the mixture with thorough mixing. The resultant solution is then made up to 250ml by adding distilled water

Preparation of Cu_2O Nanoparticles

In a typical experiment 5 mL of Benedict's solutionwasmixed with Arachishypogaealeafextract in a beaker and vigorously stirred for 15 min. After 15 minutes, the colour of the solution changed from blue to green and brick-red precipitate was produced, indicating the formation of cuprous oxide nanoparticles.The solution was kept at room temperature for evaporation of aqueous phase.

Results and Discussion

The chemical reaction which occurs

$$RCHO + 2Cu^{2+} + 2H_2O \longrightarrow RCOOH + Cu_2O +$$

In fact, the reduction of Cu^{2+} to Cu^{+} plays a main role in this process and then Cu_2O is generated through the hydrolysis of Cu^{+} according to the following reactions.

$$Cu^{2+} + H_2O \longrightarrow CuOH + H^{+}$$

$$2CuOH \longrightarrow Cu_2O + H_2O$$

Therefore, we took advantage of the ready reactivity of solution with reducing sugars to innovate a facile method for the synthesis of Cu_2O nanoparticles. The Cu_2O nanoparticles obtained by using Arachis hypogaea leaf extract was analyzed by UV-Visible spectra as shown in Figure I. The peak at 259 nm was due to inter band transition of core electrons of copper and copper oxide [I. Lisiecki and M.P. Pileni., (1993)]. The solution was brick red coloured mainly because of Cu_2O nanoparticles. This color arised may be due to an excitation of the surface plasmion vibration in the metal oxide nanoparticles.

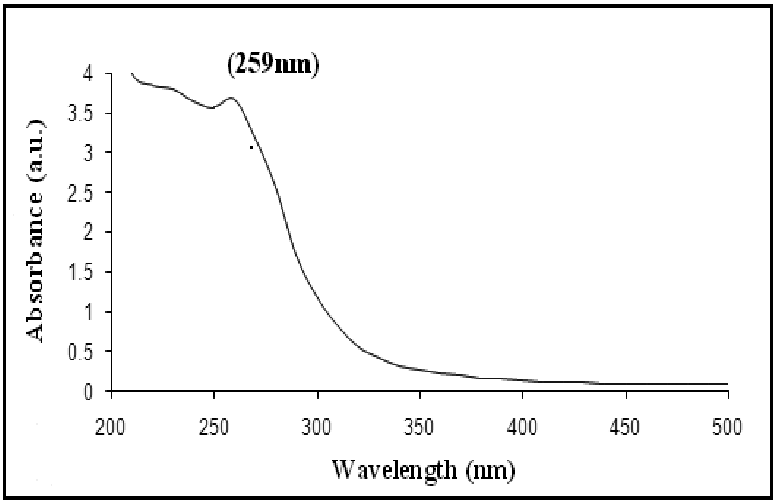

Figure I. UV-Vis spectrum of Cu_2O nanoparticles synthesized usingArachis hypogaea leaf extract

The FTIR spectra of copper oxide nanoparticles showed peaks at 3376, 1613, 1444 and 625 cm^{-1} in the region 4000–500 cm^{-1} as given in Figure II. The peaks at 1613 cm^{-1} (asymmetric) and 1444 cm^{-1} (symmetric) indicate the presence of (-COO-) carboxylate ions, responsible for formation of the Cu_2O nanoparticles. The peak at 625 cm^{-1} indicated the Cu-O vibration of Cu_2O nanoparticles [M. Kooti,and L. Matouri, (2010)].The peak at 3376 cm^{-1} is the characteristic band of hydrogen bonded OH group that may be due to the formation of nanoparticles from the aqueous phase.

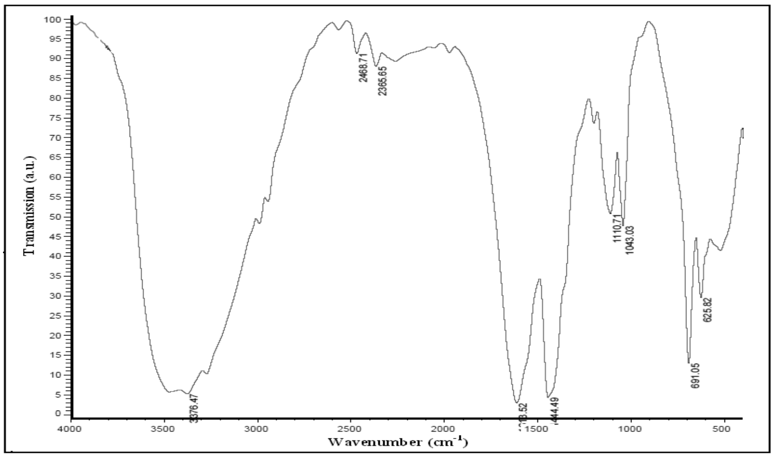

Figure II. FTIR spectrum of Cu_2O nanoparticles synthesized using Arachis hypogaea leaf extract

The XRD spectrum as given in Figure III showed three distinct diffraction peaks at 31.6°, 36.3° and 45.3° indexed as (110), (111) and (200) of the Cu_2O respectively. The average grain size of the Cu_2O nanoparticles formed in this process was estimated from the Debye-Scherrer equation and it was found to be in the range of 60-70 nm.

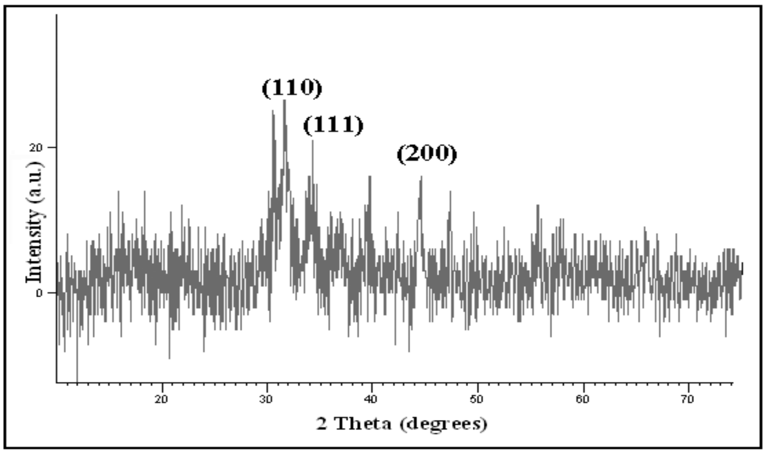

Figure III XRD pattern of Cu_2O nanoparticles synthesized using Arachis hypogaea leaf extract

The surface morphology of copper oxide nanoparticles was studied by scanning electron microscopy method as shown in Figure IV. It was observed from Figure IV that the particles were aggregated with small grains. It was also seen that the shapes of Cu_2O nanoparticles appeared like nanoneedle with rough surface.

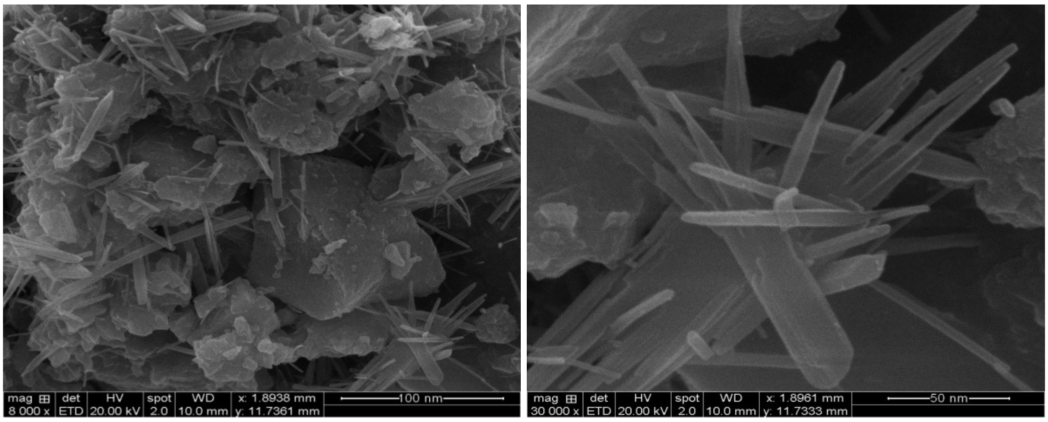

Figure IV. SEM images of Cu_2O nanoparticles synthesized using Arachis hypogaea leaf extract at different magnification levels

Conclusion

The waste leaves of Arachis hypogaea plant were utilized in the synthesis of Cu_2O nanoparticles. The reactivity of Benedict's solution with Arachis hypogaea leaf extract has been studied. The green chemistry approach addressed in the present work on the synthesis of Cu_2O nanoparticles are simple, cost effective, eco-friendly and the resultant nanoparticles are highly stable and reproducible.

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