

Synthesis and Characterization of L-ascorbic acid Stabilized Fluorescence Copper Nanoclusters

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Abstract—Copper nanostructures synthesis has been gaining attention now-a-days due to their cost effectiveness and easy availability. However, factors such as agglomeration and rapid oxidation of copper nanoparticles have made the synthesis process very difficult. In this present work we synthesized fluorescent copper nanocluster by using L-ascorbic acid as reducing as well as stabilizing agent. Synthesized copper nanocluster appears yellow in color and when seen under UV-light they showed blue color fluorescence. Further these synthesized nanoclusters were authenticated by using different characterization techniques, including fluorescence spectroscopy, UV-Transilluminator, and AFM (Atomic Force Microscopy). The synthesized nanoclusters have average diameter of around 69nm. FTIR results confirmed the complete stabilization of copper nanocluster by using L-ascorbic acid and AFM images showed that synthesized nanoparticles were in cluster form.

Keywords: Copper nanoclusters, Fluorescent nanoclusters, L-ascorbic acid

Introduction:

In the past few years, there has been an explosion of interest in the preparation and synthesis of various metal nanoparticles due to their unique optical and electronic properties (Lu et al., 2012; Hu et al., 2016; Dang et al., 2011). Synthesis of copper nanostructures now-a-days gradually became an active research area due to their low cost, good water solubility and easy availability (Ramyadevi et al., 2012). For synthesis of metal nanostructures generally two approaches are followed i.e. bottom up and top down (Hoeppener et al., 2012; Wang and Xia et al., 2004). Although, several methods have been used for the synthesis of metal nanostructures such as chemical, physical, protolytic reduction, polyol process, microemulsion, alcohol reduction, electric arc discharge, thermal decomposition, co-precipitation, sol gel method, hydrothermal methods and green synthesis (Zhu et al., 2004; Thakkar et al., 2010). Out of all listed methods chemical reduction method is most widely used for synthesis of nanostructures because of its simplicity (Sun et al., 2002).

Metal nanostructures prepared using chemical reduction method exhibit good functional properties but use of hazardous chemical agents makes the process toxic in some cases. To avoid the toxicity here we synthesized copper nanoclusters (Cu NCs) using ascorbic acid as reducing and stabilizing agent. Ascorbic acid makes the process economical, nontoxic and environment friendly. The synthesized copper nanoclusters were characterized by various techniques such as Fluorescence Spectroscopy, UV-transilluminator, AFM (Atomic Force Microscopy). Fluorescent copper nanoclusters have distinctive applications in modern science such as for targeted drug delivery in clinical trial, water purification, substrate in cancer treatment method and medication, in electronics, environment, manufacturing and material, catalysis energy harvesting (Shamaila et al., 2016; Xu et al., 2016; Rastogi et al., 2017; Athanassiou et al., 2006). They have potential use in agriculture, cosmetics, paints, food coatings, textiles, health care, material science, space industry, energy science, optoelectronics and nonlinear optical devices (Iravani, 2011; Jagathesan and Rajiv, 2018; Hu et al., 2016). Copper nanocluster are also employed successfully for the detection of various analytes such heavy metal, toxic substances, pesticides residues in food as well as in environmental samples.

Materials and Methods:

Chemicals:

Cupric Chloride (CuCl₂.2H₂O), Hydrochloric acid and Nitric acid were purchased from Thermo-Fisher Scientific India Pvt. Ltd. (Mumbai, India). L-Ascorbic Acid and Sodium Hydroxide (NaOH) were purchased from Merck Ltd. (Mumbai, India). All the listed chemicals were of analytical grade and were used without any further purification. All glassware was cleaned by aqua regia (HCL: HNO₃= 3:1 v/v). Millipore Milli-Q (18 MΩ) and distilled water was used throughout the experiment.

Synthesis of copper nanoclusters:

The aqueous solution of L-Ascorbic acid stabilized nanoclusters was synthesized by modifying a previously reported method of one pot 'green' synthesis method (Umer et al., 2015). 50 ml of 0.01 M Cupric Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was prepared and sonicated for 10 minutes, after which it was heated on a hot plate cum magnetic stirrer at exactly 85°C with vigorous stirring. The temperature was monitored throughout the experiment using a Sigma handheld IR thermometer. After the temperature was constant, 8 ml of 0.25 M L-Ascorbic acid was added dropwise post which the color of the solution changed to pale greenish-yellow. As soon as the color change was observed, the heating was stopped and the stirring continued for 12 hours. The obtained CUNCs were light green in color when observed from the naked eye and exhibit blue fluorescence when exposed to UV light.

Instrumentation:

Atomic Forced Microscopy (AFM) was executed using Bruker Multimode Scanning Probe Microscope, all fluorescence data was recorded using Perkin Elmer LS55 Fluorescence Spectrometer, FTIR spectra was obtained using Perkin Elmer FTIR-SPECTRUM 2, all UV-Visual Spectral data were recorded using ThermoScientificMultiscan GO. The temperature was monitored throughout the experiment using a Sigma hand held IR thermometer.

Results and Discussion:

Characterization of copper nanoclusters

Synthesized nanoclusters were yellow in color as seen visually with naked eyes and blue color fluorescence was observed when seen under UV-light (Figure 1). The nanoclusters were clear in color and no aggregation was observed. The AFM (Atomic Force Microscopy) results showed that synthesized copper nanoclusters were in dispersed form. Copper nanoclusters were uniformly dispersed, and had average size approximately 65 nm and the 3-D illustration of the AFM data in figure 2 describes the maximum height of the particles to be 14.4 nm. The optical properties observed by fluorescence spectroscopy, as seen in figure 3, showed the emission spectra distinctly at 455 nm with excitation wavelength being 386 nm. The Stokes shift ($\lambda_{\text{emission}} - \lambda_{\text{excitation}}$) observed is 69 nm which proves the particles have highly fluorescent property.

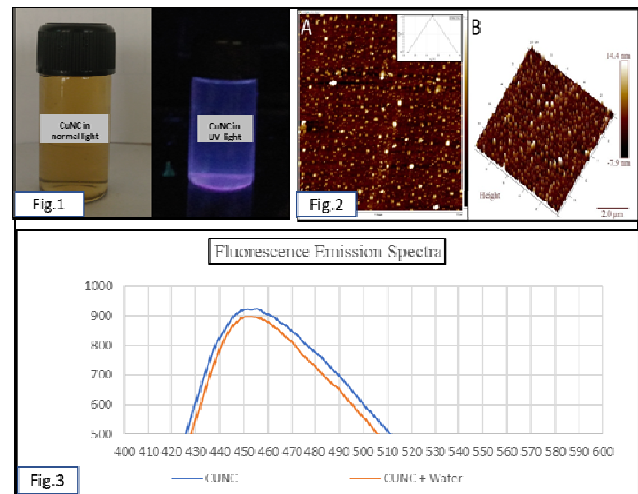


Fig. 1: A. CuNC solution as observed in daylight. B. CuNC solution as observed under UV light.

Fig. 2: A. The AFM image shows the uniformly dispersed as prepared copper nanoclusters with insert graph of average radius being 32.4 nm. B. The 3-D image shows the maximum height of the as prepared copper nanocluster's surface to be 14.4 nm.

Fig. 3: Fluorescence emission spectra of copper nanocluster.

Stability of Copper nanoclusters

The main factors that affect the use of CuNC's are the stability in the dispersion. Many stabilization agents such as Polyvinyl Pyrrolidone (PVP), Polyethylene glycol and C-TAB are used to prevent agglomeration. L-Ascorbic acid was used as a reducing agent as well as a stabilizing agent in this work to avoid contaminations of other organic compounds. The prepared CuNC's suspensions were placed without any further mixing or treatment for six weeks, and no sedimentation was seen in that period. This indicates that ascorbic acid acts as a good reducing agent as well as a stabilizing agent.

Conclusions

In this work we reported a green method for the synthesis of L-ascorbic acid stabilized fluorescence copper nanoclusters. The synthesized fluorescence copper nanoclusters colloidal solution was placed without any further mixing or treatment for six weeks, and no sedimentation was seen in that period. This indicates that L-ascorbic acid stabilized the copper nanoclusters appropriately and prevented the oxidation of nanoclusters. Our reported method of synthesis of nanoclusters is very simple, economical, and has no toxic and hazardous effect. The synthesized nanoclusters can be applied to develop the contaminant and adulterant sensor.

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References: -

- [1] Athanassiou EK, Grass RN, Stark WJ. Large-scale production of carbon-coated copper nanoparticles for sensor applications. *Nanotechnology*. 2006 Feb 27;17(6):1668.
- [2] Dang TM, Le TT, Fribourg-Blanc E, Dang MC. Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. 2011 Mar 7;2(1):015009.
- [3] Hoepfner S, Maoz R, Cohen SR, Chi LF, Fuchs H, Sagiv J. Metal Nanoparticles, Nanowires, and Contact Electrodes Self-Assembled on Patterned Monolayer Templates—A Bottom-up Chemical Approach. *Advanced Materials*. 2002 Aug 5;14(15):1036-41.
- [4] Hu X, Liu T, Zhuang Y, Wang W, Li Y, Fan W, Huang Y. Recent advances in the analytical applications of copper nanoclusters. *TrAC Trends in Analytical Chemistry*. 2016 Mar 1;77:66-75.
- [5] Iravani S. Green synthesis of metal nanoparticles using plants. *Green Chemistry*. 2011;13(10):2638-50.
- [6] Jagathesan G, Rajiv P. Biosynthesis and characterization of iron oxide nanoparticles using *Eichhorniacrassipes* leaf extract and assessing their antibacterial activity. *Biocatalysis and agricultural biotechnology*. 2018 Jan 1;13:90-4.
- [7] Jurgons R, Seliger C, Hilpert A, Trahms L, Odenbach S, Alexiou C. Drug loaded magnetic nanoparticles for cancer therapy. *Journal of Physics: Condensed Matter*. 2006 Sep 8;18(38):S2893.
- [8] Kelly KL, Coronado E, Zhao LL, Schatz GC. The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment 2003.
- [9] Ramyadevi J, Jeyasubramanian K, Marikani A, Rajakumar G, Rahuman AA. Synthesis and antimicrobial activity of copper nanoparticles. *Materials letters*. 2012 Mar 15;71:114-6.
- [10] Rastogi A, Zivcak M, Sytar O, Kalaji HM, He X, Mbarki S, Brestic M. Impact of metal and metal oxide nanoparticles on plant: a critical review. *Frontiers in chemistry*. 2017 Oct 12;5:78.
- [11] Shamaila S, Zafar N, Riaz S, Sharif R, Nazir J, Naseem S. Gold nanoparticles: an efficient antimicrobial agent against enteric bacterial human pathogen. *Nanomaterials*. 2016;6(4):71.
- [12] Sun Y, Xia Y. Shape-controlled synthesis of gold and silver nanoparticles. *Science*. 2002 Dec 13;298(5601):2176-9.
- [13] Thakkar KN, Mhatre SS, Parikh RY. Biological synthesis of metallic nanoparticles. *Nanomedicine: nanotechnology, biology and medicine*. 2010 Apr 1;6(2):257-62.
- [14] Thakkar KN, Mhatre SS, Parikh RY. Biological synthesis of metallic nanoparticles. *Nanomedicine: nanotechnology, biology and medicine*. 2010 Apr 1;6(2):257-62.
- [15] Umer, A., Naveed, S., Ramzan, N., Rafique, M.S. and Imran, M., 2014. A green method for the synthesis of Copper Nanoparticles using L-ascorbic acid. *Matéria (Rio de Janeiro)*, 19(3), pp.197-203
- [16] Wang Y, Xia Y. Bottom-up and top-down approaches to the synthesis of monodispersed spherical colloids of low melting-point metals. *Nano letters*. 2004 Oct 13;4(10):2047-50.
- [17] Xu Q, Zhao Y, Xu JZ, Zhu JJ. Preparation of functionalized copper nanoparticles and fabrication of a glucose sensor. *Sensors and Actuators B: Chemical*. 2006 Mar 30;114(1):379-86.
- [18] Zain NM, Stapley AG, Shama G. Green synthesis of silver and copper nanoparticles using Ascorbic acid and Chitosan for antimicrobial applications. *Carbohydrate polymers*. 2014 Nov 4;112:195-202
- [19] Zhu J, Liu S, Palchik O, Koltypin Y, Gedanken A. Shape-controlled synthesis of silver nanoparticles by pulse sonoelectrochemical methods. *Langmuir*. 2000 Aug 8;16(16):6396-9.