Green Luminescent Copper Nanoparticles

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Abstract: Copper nanoparticles are synthesized by a green chemical reduction method using Gum Kondagogu extract as stabilizer. The as-prepared powder samples are characterized by Transmission Electron Microscopy (TEM), Small Angle X-Ray Scattering (SAXS), UV-Visible Spectroscopy, X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The as-prepared copper nanoparticles are found to be FCC crystalline and nearly monodispersed with particles size 19 nm. Photoluminescence (PL) measurement showed strong green visible emission and PL intensity was found enhanced with the presence of natural extract on copper nanoparticle surface. The increase in the PL intensity was mainly due to copper nanoparticles. Photoluminescence spectra of copper nanoparticles show an emission peak at 430 nm when illuminated at 325 nm.

Keywords: green synthesis, copper nanoparticles, TEM, photoluminescence

1. Introduction
Nanoparticles have significant applications in various fields such as textiles, renewable energy, environment, biomedical and healthcare etc. The environmentally friendly nanoparticles synthesis methods are becoming increasingly popular and are much needed due to worldwide problems associated with environmental contamination. Different preparation methods such as UV irradiation, laser ablation, lithography, aerosol technologies and photochemical reduction techniques have been successfully used to produce various nanoparticles. But these methods are expensive and involve the use of harmful chemicals. Therefore, there is a significant interest in the development of eco-friendly nanoparticle synthesis routes [1-10]. Although luminescence in metal nanoparticles is known for long time, it has received very limited study. Normally metals like copper exhibit visible photoluminescence due to their surface enhanced optical phenomenon and the sp-conduction band to d-band transition in metals is mainly responsible for it [11]. Metals with free electrons such as Au, Ag, Cu and alkali metals have plasmon resonance in the visible spectrum, which causes intense colors. Further the surface plasmons promote interband transitions which result in additional emission [12-14].

Great attention has been paid to copper nanoparticles among other metal nanoparticles due to their unusual properties besides the fact that they are cheaper and have high conductivity. The general problems like aggregation and oxidation of copper nanoparticles limit their usage. However, the usage of suitable separate stabilizing agent in the preparation rectifies this problem easily. The simple and low cost chemical reduction method is highly preferred for the preparation of copper nanoparticles though many synthesis methods are available [15]. The 3d and 4sp conduction electrons in the electronic structure of copper are important in the exhibition of its photoluminescence behavior. In the present work, we have tested the capping behavior of Gum Kondagogu extract to surround copper nanoparticles.
and also the impact of Gum Kondagogu extract in enhancing the photoluminescence behavior of copper nanoparticles [16-31].

2. Experimental

Gum Kondagogu is a natural gum found in the exudates from the tree Cochlospermum Gossypium. The major functional groups identified in the Gum Kondagogu are hydroxyl, acetyl, carbonyl and carboxylic groups. Gum Kondagogu samples were collected from Girijan Co-operative Corporation, Government of Telangana Undertaking, Hyderabad, India. Gum Kondagogu was powdered to obtain a fine and uniform sample. Later it was accurately weighed (4 g), and a clear Gum Kondagogu solution is prepared. The as-prepared solution was freeze-dried and stored until further use for preparation of copper nanoparticles. A simple two stage chemical reduction method was employed to synthesize copper nanoparticles in which copper salt (precursor) is initially reduced by Hydrazine Hydrate (HH, reducing agent) and then stabilized by Gum Kondagogu extract (stabilizing agent). In addition, L-Ascorbic acid was used as an anti-oxidant agent and NaOH was used as a catalyst and also to adjust the pH to 12. The solutions of Copper nitrate (0.04M), L-Ascorbic acid (0.001M) and Gum Kondagogu extract (50 mL) were prepared separately using Millipore water. In the beginning of process, the solutions of Gum Kondagogu extract and L-Ascorbic acid were added to copper nitrate solution while stirring. Then the solutions of HH (1 M) and NaOH (0.01 M) were added to the mixed copper salt solution under rapid stirring. Stirring was continued for 1hr during which initial blue color of the reaction mixture turns finally in to brown-black color. The resultant precipitate was washed twice and dried to obtain copper nanoparticles.

2.1. Capping mechanism of copper nanoparticles

Water soluble polymers increase the bulk phase viscosity and as a result of this the particles contain lower kinetic energies leading to the reduction of collisions eventually. In water soluble polymers surface and interfacial tensions raise to affect the particle size and the rate of coalescence due to the presence of high proportion of acetyl groups (– COOCH3) that imparts an amphipathic character to the molecule. The stabilization of copper nanoparticles was summarized as following. (1) Cu²⁺ ions are reduced to Cu⁰ atoms (2) Cu atoms form clusters through hydrophobic to hydrophilic driven reactions and metal bonding. (3) The natural extract was used to control Cu cluster from aggregation.

2.2. Characterization

Transmission Electron Microscope (TEM-Phillips equipment) was utilized to study the morphology and particle size of as-prepared green copper nanoparticles. Panalytical X-ray Generator (PW 3830) having SANS 896986 Anton Paar mounted on it was used to obtain the Small Angle X-Ray Scattering (SAXS) data to find the particle size of as-prepared nanoparticles. The surface plasmon peak is studied by using the UV-Visible spectrometer (Lab India Instruments Pvt. Ltd, Lab India UV- 3000+). Philips X-ray diffractometer coupled with graphite monochromer is used to obtain X-Ray Diffraction (XRD) pattern of as-prepared copper nanoparticles. Williamson – Hall equation was used to evaluate the crystallite size of as-prepared copper nanoparticles given as following.

\[ 
\beta_{hkl} \cos \theta = \frac{K \lambda}{D} + 4\varepsilon \sin \theta 
\]

where D is the diameter (crystallite size) of the particle \( \lambda \) is the wavelength of X-rays. FTIR spectrometer (Bruker Optics, Germany, Tensor 27) was used to obtain Fourier Transform Infrared (FTIR) spectra of as-prepared copper nanoparticles by KBr pellet method. Fluorolog 3-11 Spex – Jobin Yvon spectrofluorometer was used get the fluorescence spectra where Xenon lamp source was used for excitation.

3. Results and Discussion

TEM is used to study the morphology and particle size of as-prepared copper nanoparticles. TEM image, SAED patterns and particle size distributions of as-prepared copper nanoparticles stabilized by Gum Kondagogu extract are given in Figure 1. All the TEM images show that most of the nanoparticles are nearly spherical and have polycrystalline nature as there are distinct contrast regions within one nanoparticle. The values of average diameter and interplanar spacing are calculated using Image J software. The particle size of copper nanoparticles from TEM image is determined to be 19 nm.
The SAED pattern (Figure 1) displays four diffraction rings whose interplanar spacing values are found to be 0.2, 0.18, 0.13, and 0.11 nm. These results indicate the FCC crystalline nature of Cu (JCPDF no. 71-4610, Fm-3m, \( a = 0.3617 \) nm, \( d_{111} = 0.20883 \) nm, \( d_{200} = 0.18085 \) nm, \( d_{220} = 0.12788 \) nm, \( d_{311} = 0.10906 \) nm) [32]. Further the particle size distribution (Figure 1) confirms that the majority of nanoparticles are in the range of 1 – 10 nm. However, there are very few nanoparticles of other higher particle sizes indicating that the samples consist of slightly wide size distribution of copper nanoparticles.

![SAED pattern and particle size distribution](image1)

**Figure 1.** TEM image, SAED pattern and particle size distribution of Gum Kondagogu extract stabilized copper nanoparticles

SAXS studies are carried using Mo and Cr radiations with three different configurations to cover wide q-range. The SAXS intensity profiles of as-prepared copper nanoparticles stabilized by Gum Kondagogu extract are displayed in Figure 2 which shows distinct power law regimes.

![SAXS image](image2)

**Figure 2.** SAXS image of Gum Kondagogu extract stabilized copper nanoparticles
The variation of I (q) with q has been obtained after subtracting the background scattering pattern of aqueous solution of the stabilizing polymer. SAXS analysis indicates that the average particle size of copper nanoparticles prepared from copper nitrate is around 2.04 nm. Although, the log–log SAXS plots show three power law regimes, they most probably represent a polydisperse trimodal size distribution of fractal objects. The Guinier regions and a Porod region give the ensemble average dimensions of these objects.

UV visible absorption spectroscopy is used to determine the formation, shape and stability of copper nanoparticles in aqueous solutions. The UV absorption spectrum of as-prepared copper nanoparticles stabilized by Gum Kondagogu extract is recorded as shown in Figure 3 which exhibits an absorption peak at approximately 558 nm. The absorption of copper nanoparticles is responsible for this peak. The protecting effect of the surfactant increases with the concentration and favors formation of smaller NPs of copper network. The broadness of the absorption spectra can be attributed to the polycrystalline nature and also agglomeration nature of nanoparticles of the sample as is observed from TEM and SAXS analysis. It is possible that, due to aggregation and agglomeration, particle size increases and material gets settled down at the bottom of container causing decrease in the absorbance. But, the stabilizer Gum Kondagogu that surrounds the copper nanoparticles protects it from further aggregation and agglomeration. The amino acids, Proteins and polysaccharides present in Gum Kondagogu extract are responsible for the reduction and stabilization of copper nanoparticles.

As copper metal gets oxidized immediately after the reduction, the Gum Kondagogu alone is not sufficient for the reduction of copper salts followed by the stabilization of the copper ions. This is the reason why a separate agent HH is used for reducing the copper salt. The Gum Kondagogu is now only used as stabilizing agent during the synthesis of copper nanoparticles.

![Figure 3](image)

Figure 3. UV visible absorption spectrum of Gum Kondagogu extract stabilized copper nanoparticles

XRD is used for the phase identification of copper samples and the XRD pattern of as-prepared copper nanoparticles stabilized by Gum Kondagogu extract is recorded as shown in Figure 4. XRD pattern displays Cu characteristic diffraction peaks at around 2θ = 43°, 50°, 74° corresponding to (111), (200), (220) planes of FCC Cu crystals (JCPDS No.04-0784). The lattice parameter ‘a’ is calculated using these profiles as 0.363 nm and this value is consist with the reported value 0.3615 nm. Further the average crystallite size of as-prepared copper nanoparticles is determined as 6 nm by using equation (1).

The information derived from TEM, SAXS, UV and XRD results indicate that all of the selected methods are helpful in making an accurate and complete characterization of the nanopowder [33].
FTIR measurements are performed to study the responsible molecules for capping and reducing agent and FTIR spectrum exhibit various bands that are characteristic of stretching and bending vibrations of O-H, C=C and C-O functional groups [12-13]. The FTIR spectra of Gum Kondagogu extract stabilized copper nanoparticles prepared from copper nitrate and pure Gum Kondagogu extract are recorded as shown in Figure 5.

The FTIR spectrum of Gum Kondagogu extract stabilized copper nanoparticles consists of two broad and strong bands along with two weak bands in the region 3600–2800 cm\(^{-1}\). Broad and strong bands centered at around 3450 cm\(^{-1}\) and 617 cm\(^{-1}\) are related to O-H stretching frequency and the weak bands centered at around 2928 cm\(^{-1}\) and 2855 cm\(^{-1}\) are related to C-H stretching. The broad band observed at around 3450 cm\(^{-1}\) and 617 cm\(^{-1}\) illustrates the stretching frequency of hydroxyl group (OH group) present on the surface of the copper nanoparticles that characterizes stretching vibrations of O-H bonds in H\(_2\)O molecules adsorbed on the nanoparticle surface. But it could be related also with the copper hydroxide presence.

In addition, the two absorption peaks appeared at around 1565 cm\(^{-1}\) and 1622 cm\(^{-1}\) are due to O-H bending and the peak observed at around 1411 cm\(^{-1}\) is related to –O-C-O- symmetric stretching. Further, a band observed at around 1312 cm\(^{-1}\) corresponds to –C–C–H deformation. A noticeable shift to higher
frequencies and change in intensities of peaks is observed in the range 1000–2000 cm\(^{-1}\) of the spectra of copper nanoparticles when compared to that of Gum Kondagogu extract. This can be attributed to the change in their population because of electrostatic interaction with Cu\(^0\) and also optimized concentration of reducing agent.

For pure Gum Kondagogu extract, peaks in the range of 650-1000 cm\(^{-1}\) are attributed to C-H bending vibrations and peaks in the range of 1300-1450 cm\(^{-1}\) are ascribed to C-H stretching vibrations of –HC-CH- links of Gum Kondagogu extract molecules. Also, the band observed at around 981 cm\(^{-1}\) is related to C-O stretching, which is the characteristic of either functional moiety. The peaks in the range 650-1000 cm\(^{-1}\) of copper nanoparticles are shifted slightly to higher wave numbers compared to that of FTIR spectrum of Gum Kondagogu extract. These differences indicate that the thin layer of Gum Kondagogu extract molecule is developed on the surface of the copper nanoparticles.

The copper nanoparticles surrounded by natural stabilizer Gum Kondagogu extract are stable for about 25 days and have shown no contamination during this period. However, the copper nanoparticles washed in hot water have shown contamination with copper oxide. This is because of the thin Gum Kondagogu extract layer removed when they are washed in hot water. This observation confirmed that the natural extract molecules on the surface of copper nanoparticles are important to avoid oxidation. As natural extract layer surrounded the copper nanoparticles, the prepared copper nanoparticles are useful in medical area.

The photoluminescence spectrum of as-prepared copper nanoparticles stabilized by Gum Kondagogu extract is displayed in Figure 6. The obtained spectrum has exhibited an emission peak at around 430 nm when excited at around 325 nm by using Xenon laser. The radiative recombination of electron hole pair between d-band and sp-conduction band followed by initial electronic relaxation is responsible for this photoluminescence behavior. Six bands are created by the valence electrons (d & s) of the atoms of the copper nanoparticles out of which five bands (d-bands) lie below the Fermi level and the sixth band (conduction band or sp band) lies above the Fermi level.

![Figure 6. PL Spectrum of Gum Kondagogu extract stabilized copper nanoparticles](image)

An energy level diagram (Figure 7) is constructed based on the experimental results obtained for as-prepared copper nanoparticles where \(E_0\) is the ground state and \(E_1, E_2\ldots\) etc. are the excited states. Transitions take place from \(E_0\) to \(E_1, E_2\ldots\) etc. in accordance with the excitation energy. An excited electron de-excites non-radiatively to the lowest excited state prior to photon emission, in a time short enough compared to photon emission time. De-excitation to the 3d level yields fluorescence emission as shown in Figure 7.

The fluorescence of molecules in direct contact with the copper gets enhanced. It has been understood that the adsorbed natural extract on the surface of copper nanoparticles influences in enhancing the emission peak along with the shifting of its position. In addition, the emission properties of the fluorescent molecules near a copper nanoparticles change significantly.
Conclusions

Copper nanoparticles prepared from the present approach are found to be stable for about 25 days and this rapid synthesis approach will surely enhance the advantages of copper nanoparticles in view of various applications. The photoluminescence spectrum of as-prepared copper nanoparticles stabilized by Gum Kondagogu extract has exhibited an emission peak at 430 nm. The enhancement of photoluminescence spectra is attributed to the fluorescence of molecules in direct contact with the natural extract capped copper metal.

References

[1] BD.Chithrani, AA.Ghazani, WCW.Chan. Nano Lett. 2006; 6, 662.
[2] AA.Athawale, PP.Katre, M.Kumar Mater Chem Phys. 2005; 91, 507.
[3] C.Charton, M.Fahlman. Surf Coat Technol. 2003; 174, 181.
[4] Z.Duan, G.Ma, W.Zhang. Bull. Korean Chem. Soc. 2012; 33, 12, 4003.
[5] F.Figueras, BJ.Coq. Mol. Catal. A: Chem. 2001; 173, 223.
[6] CJ.Flytzanis. Physics B, At. Mol. Opt. Phys. 2005; 38 S661.
[7] JJ.Guang, Y.S. Hai, T.C. Bo, H. Jing, T.M. Tang. Trans. Nonferrous Met. Soc. China 2007; 17.
[8] SK.Ghosh, T.Pal Chem. Rev. 2007; 107, 4797
[9] PK.Hansma, HP.Broida. Appl. Phys. Lett. 1978; 32, 545.
[10] J.Hassan, M.Sevignon, C.Goazzi, E.Schulz, M.Lemaire. Chem. Rev. 2002; 1021359.
[11] S. Annapurna, Y. Suresh, B. Sreedhar, G. Bhikshamaiah, A.K.Singh. Photoluminescence of Green Synthesized Copper Nanoparticles. Tech Connect Briefs 2015, TechConnect.org, 265-268, ISBN: 978-1-4987-4727-1
[12] Sathiraju Annapurna, Yathapu Suresh, Bojja Sreedhar, Ganganishetti Bhikshamaiah, A.K.Singh. Characterization of Green Synthesized Copper Nanoparticles Stabilized by Ocimum Leaf Extract. Mater.Res.Soc.Symp.Proc.Vol.1704@2014Materials Research Society, DOI: 10.1557/opl.2014.806.
[13] Suresh Y, Annapurna S, Bhikshamaiah G, and A.K.Singh. Characterization of Green Synthesized Copper Nanoparticles: a Novel Approach. Proceedings of the “International Conference on Advanced Nanomaterials & Emerging Engineering Technologies” (ICANMEET-2013), 2013; 978-1- 4799-1379-4/13/IEEE.
[14] Y.Suresh, S.Annapurna, A.K.Singh, A.Chetana, Chand Pasha, G.Bhikshamaiah. Characterization and Evaluation of Anti-biofilm Effect of Green Synthesized Copper Nanoparticles. Materials Today: Proceedings, 2016; 3, 1678.
[15] Y. Suresh, S. Annapurna, A. K. Singh, G. Bhikshamaiah. Green Synthesis and Characterization of Tea Decoction Stabilized Copper Nanoparticles. International Journal of Innovative Research in Science, Engineering and Technology. 2014; 3, 4, 11265.

[16] TS. Iwayama, DE. Hole, PD. Townsend. J. Luminescence, 1999; 80, 235.

[17] T. Joseph, KV. Kumar, AV. Ramaswamy, SB. Halligudi. Catal. Commun. 2007; 8, 629.

[18] PK. Khanna, S. Gaikwad, PV. Adhyapak, N. Singh, R. Marimuthu. Mater. Lett. 2007; 61 (25), 4711.

[19] PS. Kumar, KL. Rai. Chemical Papers 2012; 66, 772.

[20] V. Mohanraj, Y. Chen. Nanoparticles-a review. Trop J Pharm Res. 2007; 5, 561.

[21] Mooradian, Phys. Rev. Lett. 1969; 22, 185.

[22] B. Pergolese, M. Muniz-Miranda, A. Bigotto. J. Phys. Chem. B. 2006; 110 9241.

[23] VG. Plekhanov, TV. Siliukova. Sov. Phys. Solid State. 1990; 32, 1268.

[24] S. Ranjit, Z. Duan, P. Zhang, X. Liu. Org. Lett. 2010, 12, 4134.

[25] S. Reymond, J. Cossy. Chem. Rev. 2008; 108, 5359.

[26] MH. Samim, NK. Kaushik, A. Maitra. Bull. Mater. Sci. 2007; 30, 5, 535.

[27] OP. Siwach OP, Sen P. J. Nanopart. Res. 2008; 10, 107.

[28] Ya B. Sokovets, A. Ya. Khairellina, Babenko, J Applied Spectrosc. 2006; 73 (4), 576.

[29] X. Wang, J. Zhuang, Q. Peng, Y. Li. Nature 2005; 437, 121.

[30] JP. Wilcoxon, JE. Martin, F. Parsapour, B. Wiedeman, DF. Kelley. J. Chem. Phys. 1998; 108, 9137.

[31] H. Zhu, C. Zhang, Y. Yin. Nanotechnology 2005; 16, 3079.

[32] G. Cheng, A. R. Hight Walker. Transmission electron microscopy characterization of colloidal copper nanoparticles and their chemical reactivity, Anal Bioanal Chem. 2010; 396, 1057.

[33] R. Kalyanaraman, S. Yoo, M. S. Krupashnkara, T. S. Sudarshan, and R. J. Dowding, Synthesis and Consolidation of Iron Nanopowders, Nanostructured Materials, 1998; 10, 8, 1379.