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Synthesis of Linoleic Acid Capped Copper Nanoparticles and Their Fluorescence Study

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Abstract Copper nanoparticles have been prepared through the reduction of cupric ions by ethanol with linoleic acid as a capping agent. The morphology and structure of these nanoparticles have been investigated using transmission electron microscopy. The X-diffraction study shows that the nanoparticles are crystalline and mainly composed of face-centered cubic (fcc) copper with a narrow size distribution having an average size of 5 nm. Fluorescence spectra of these copper nanoparticles have been analysed which show two emission peak at 450 nm and 625 nm corresponding to the large energy band and small energy band respectively, when illuminated at 250 nm of an optical source.

Keywords Reduction · Linoleic acid · Absorption spectra · Fluorescence spectra

Introduction

Metal nanoparticles display many interesting optical, electronic, magnetic, mechanical and chemical properties yielding applications in nanodevices, biological nanosensors, nanoelectronics, information storage and catalysis [1]. The study of these small particles (1–100 nm) has attracted great interest because they bridge the properties of atoms and nanoparticles (1–100 nm) and even to the bulk [1–9]. Amongst many noble metals (Au, Ag, Pd, Pt), copper and copper based compounds are the most important materials because metallic copper plays a significant role in modern electronics circuits due to its excellent electrical conductivity and low cost nanoparticles [10]. So Cu will gain increasing importance as it will be an essential component in the future nanodevices due to its excellent conductivity as well as good biocompatibility [11]. In contrast with noble metals, such as silver and gold, the synthesis of copper nanoparticles is much more challenging, since copper nanoparticles are fairly unstable in aqueous solution. When copper nanoparticles are exposed to air, surface oxidation occurs and ultimately aggregation takes place in a short time. To avoid oxidation, the reduction methods are usually performed under an inert atmosphere [12], in organic solvents [13] and in presence of protective polymers [14]. Here we have prepared copper nanoparticles by reduction method [15], which is a useful method to stabilise copper nanoparticles for long time. Linoleic acid has been employed to stabilize the copper nanoparticles by capping them. The prepared copper nanoparticles have been dispersed in chloroform and then examined using X-ray diffraction (XRD), Transmission Electron Microscope (TEM), UV/Vis absorption spectroscopy (UV–vis), FTIR spectroscopy and Flourescence (FL). These nanoparticles have been prepared to study their light emission phenomenon, when excited with a particular wavelength of an optical source.

Materials and Methods

Stable copper nanoparticles can be obtained through the reduction of cupric ions by ethanol at temperature between 100 °C to 120 °C under atmospheric conditions in presence of linoleic acid and sodium linoleate [15]. In this synthesis process, 10 ml of aqueous solution containing copper chloride (0.25 g of $CuCl_2$), 0.5 g sodium linoleate (C_{18}

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H$_{32}$ONa), 5 ml ethanol (C$_2$H$_5$OH) and 1 ml linoleic acid (C$_{18}$ H$_{32}$ O$_2$) are added in a capped tube under stirring. The system is kept at the temperatures between 100 °C to 120 °C for 2 h. In the aqueous solution of copper chloride, sodium linoleate and the mixture of linoleic acid and ethanol are added in order. Three phases, a solid phase of sodium linoleate, a liquid phase of ethanol and linoleic acid, and water ethanol solution phase containing cupric ions, formed in the system. A phase transfer process of cupric ions takes place continuously across the interface of sodium linoleate and water ethanol solution due to ion exchange. This process makes a way for the formation of copper linoleate and entering of sodium ions into the acqueous phase. Then ethanol in the liquid and solution phases reduced cupric ions into copper nanoparticles. The linoleic acid caps the copper nanoparticles along with the reduction process thereby stabilizing the nanoparticles electrostatically. After cooling to room temperature, copper nanoparticles are dispersed in chloroform to form a homogenous solution of copper nanoparticles. Copper nanoparticles dispersed in chloroform show light greenish colour as shown in the Fig. 1(a) with the chemical structure of linoleic acid as shown in Fig. 1(b). The role of linoleic acid is to protect the copper nanoparticles from agglomeration by making a layer over it with its alkyl chains on the outside giving a hydrophilic surroundings to the nanoparticles and thereby the produced nanoparticles gain a hydrophobic surfaces [15]. The most important factor in this reduction method is that linoleic acid capped copper nanoparticles dispersed in chloroform remain stable for 20 days, which has been confirmed from TEM analysis, UV–vis study, and Fluorescence spectroscopy.

Result and Discussion

XRD Study

The structure of prepared copper nanoparticles has been investigated by Bruker AXS model X-ray diffractometer. The XRD patterns of the sample prepared by the present reduction method are shown in the Fig. 2.

The XRD pattern clearly indicates crystallinity of the particles as the peaks at 43.2° and 50.4° match with those of a face centred cubic (fcc) Cu as in JCPDS (Joint Committee on Powder Diffraction Standard) correspond to the planes of (111) and (220) respectively. From this study, measuring the line broadening at 43.2° and 50.4°, average particle size is estimated by using Debye-Scherrer formula [16–19]. Considering the instrumental broadening at 43.2° and 50.4° as 0.00431 and 0.00621 respectively, the average particle size is calculated to be around (5±1) nm with 9% error in the measurement.

TEM Image Analysis

Size and shape of the copper nanoparticles has been obtained from TEM micrograph, which was performed on a JEM 1000 C X II model instrument. TEM micrograph of the prepared linoleic acid capped copper nanoparticles is shown in Fig. 3(a) with a graphic of statistical size distribution of particles in Fig. 3(b). High Resolution Transmission Electron Microscopic (HRTEM) image of the same copper nanoparticles is shown in Fig. 3(c). These micrographs show that copper nanoparticles are spherical in shape with a smooth surface morphology having an average size of 5 nm. This TEM images also suggests that no clustering of nanoparticles takes place and these nanoparticles are well separated from each other with a very narrow size distribution (1–10 nm).
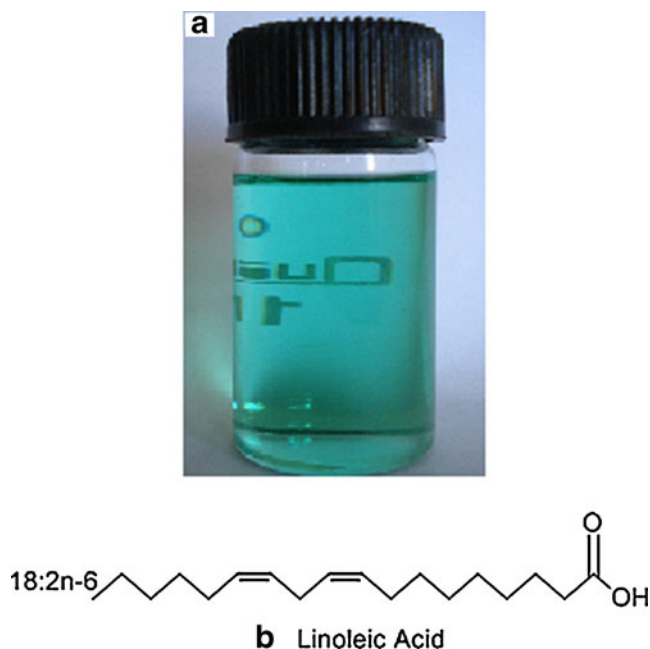

Fig. 1 a Copper nanoparticles dispersed in chloroform showing light greenish colour. b Chemical structure of linoleic acid
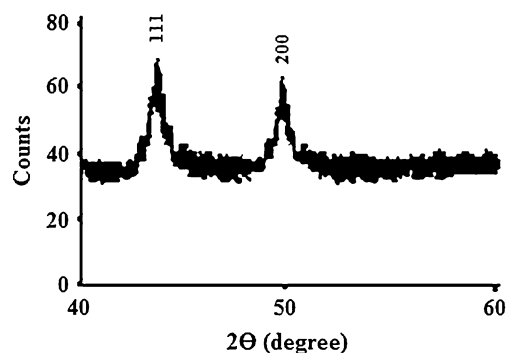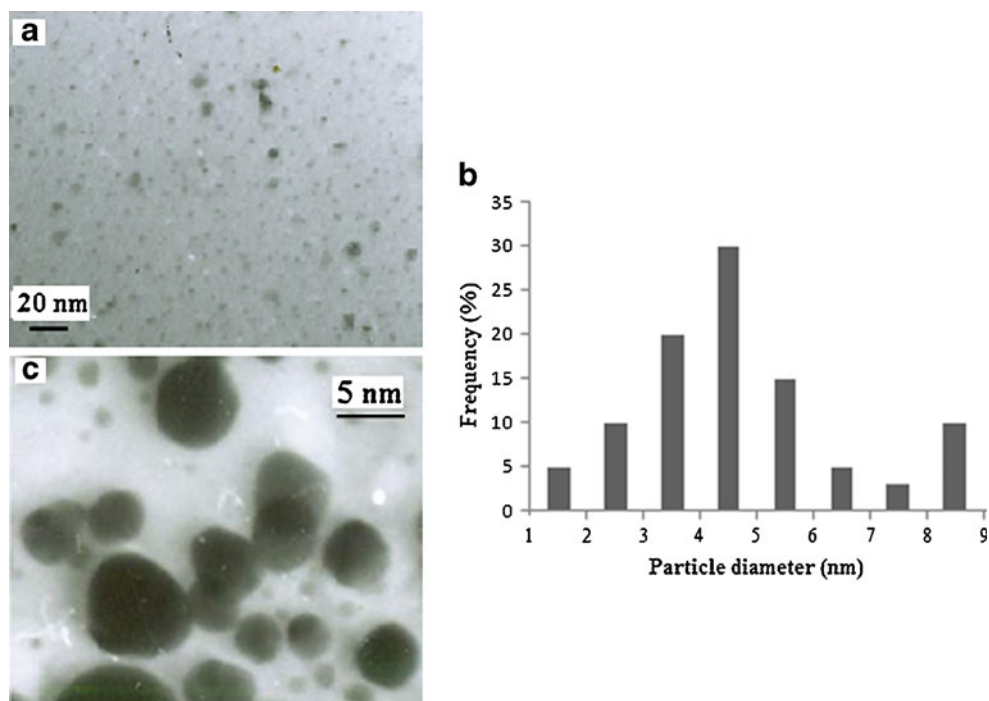

Fig. 2 XRD pattern of copper nanoparticles

Fig. 3 **a** TEM image of Copper nanoparticles. **b** Graphic for particle size distribution. **c** HRTEM image of copper nanoparticles

Analysis of FTIR Spectroscopy

The conformational structure of the linoleic acid capped Cu nanoparticle has been examined by FTIR spectroscopy. The FT-IR absorption spectra of the samples are shown in Fig. 4 with resolution of 4 cm^{-1}, which was performed in Spectrum BX series. The peak in 3,439 cm^{-1} of the FTIR spectra contains OH stretching modes [20, 21].

The peak around 3,019 cm^{-1} is due to C=C stretching mode. The lack of broad peak due to OH stretching of the free ligand in the range 3,000 cm^{-1} to 3,100 cm^{-1} is due to the chemisorptions of linoleic acid on the Cu nanoparticles. The antisymmetric and symmetric stretching at 2,930 cm^{-1} and 2,857 cm^{-1} is an indicator for the conformational ordering of the metal-linked alkyl chains of linoleic acid [22, 23].
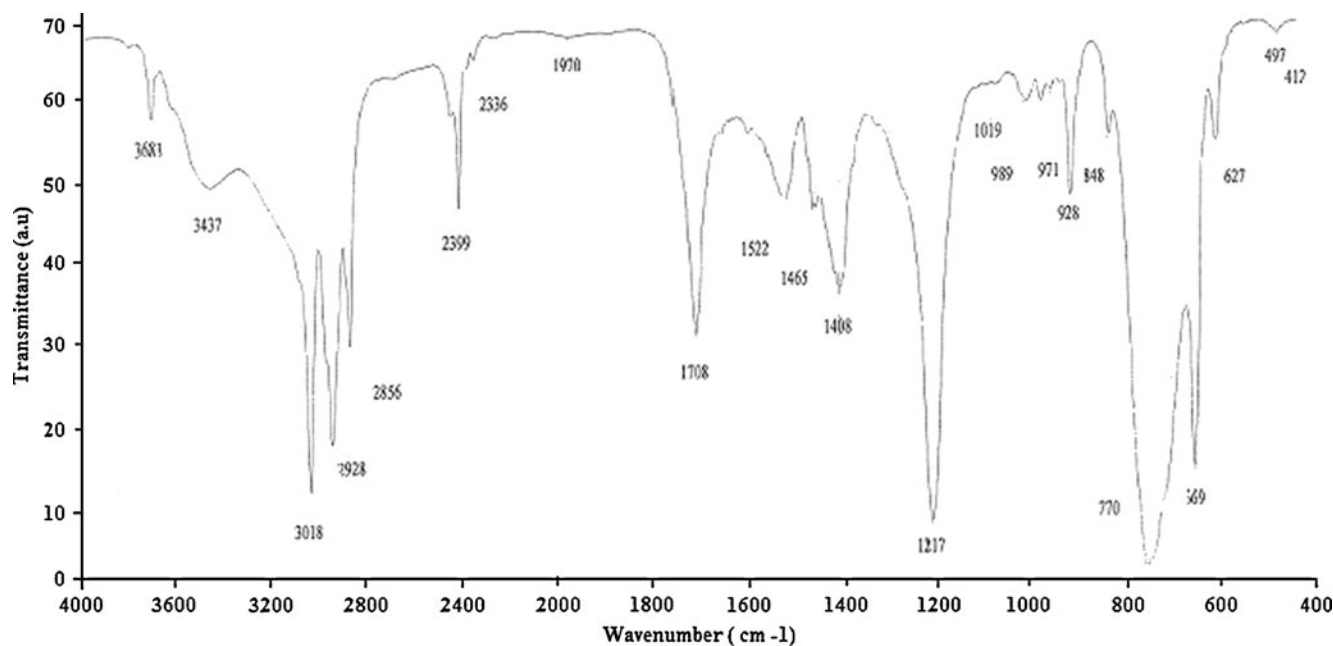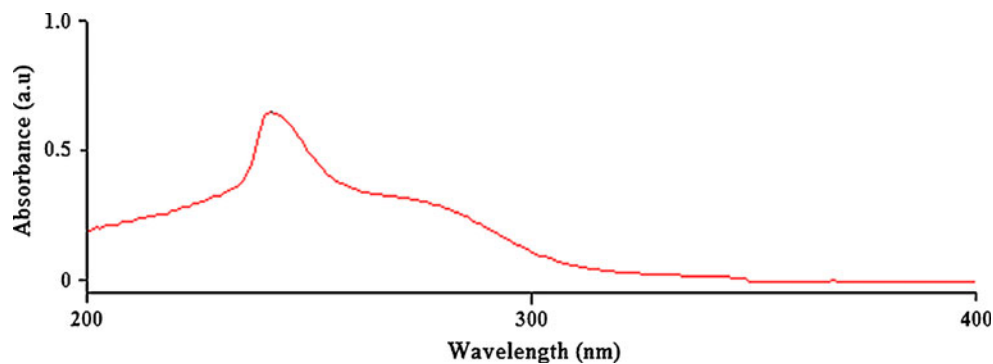

Fig. 4 FT-IR spectra of linoleic acid protected copper nanoparticles dispersed in chloroform

Fig. 5 UV- Vis spectra of copper nanoparticles

The FTIR spectra reported in Fig. 4 has been obtained for linoleic acid protected Cu nanoparticles immediately after synthesis, but it does not differ appreciably from the FTIR spectra recorded for the same nanoparticles after 20 days of storage at room temperature dispersed in chloroform.

Analysis of UV/Vis Spectroscopy

Colloidal dispersion of metal exhibits absorption bands or broad regions of absorption in the ultra violet-visible range [1–4]. Width of the absorption band and wavelength corresponding to the absorption peak strongly depend on size, shape, dielectric constant of metal nanoparticle as well as on the surrounding medium [1–9, 24–26]. This absorption is due to the excitation of surface plasmon resonance (SPR) and is a characteristic property of the metallic nature of the particle. Surface plasmon resonance is due to the collective oscillation of free electrons of the metal nanoparticles in resonance with the frequency of the lightwave interacting with the metal nanoparticles [1–9, 17–19, 24–26]. Nanosized Cu particles (size >20 nm) typically exhibit a surface plasmon resonance peak at around 560 nm [27, 28]. On the contrary, UV/Vis absorption spectra of the prepared linoleic acid capped copper nanoparticles (average size of 5 nm) dispersed in chloroform show a featureless Mie scattering profile without the appearance of SPR [29] as shown in the Fig. 5. The absorption peak in the UV/Vis
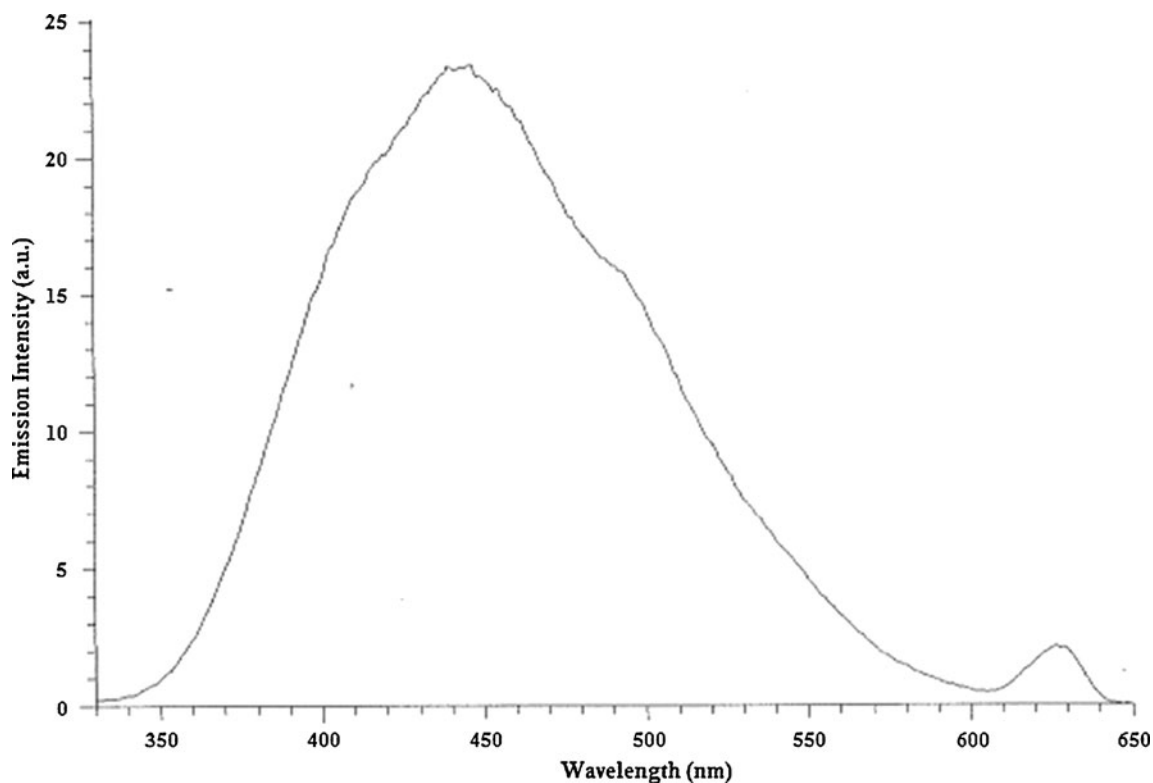

Fig. 6 Flourescence spectra of copper nanoparticles

spectra, which was performed on Perkin Elmer Lambda 351.24 model, is obtained at 241 nm and is in good agreement with the others results [29–31]. Linoleic acid capped copper nanoparticles dispersed in chloroform show light greenish colour due to this absorption. A good symmetry of the absorption spectra around the peak position indicates the narrow distribution of the particles produced, which has also been confirmed from TEM micrograph.

Flourescence Spectroscopy

In noble metal nanoparticles, the energy band splits into a series of energy levels in terms of the quantum size effect [30]. Further, the splitting of energy levels will be more distinct as the size of the nanoparticles becomes smaller [30]. The relationship between level spacing (δ) and particle size is given by $\delta \propto 1/d^3$, where d is the particle size (for a spherical particle) [32, 33]. So the energy level splitting makes the electronic transition abundant in nanoparticles. As collective oscillation of electrons (SPR) is no longer available for dissipating the incident energy, so transition from discrete valence states to excited states takes place in the Cu nanoparticle atoms [30].

In case of copper, 3d valence and 4sp conduction electrons play the role for fluorescence. The outermost d and s electrons of all the constituent atoms of the nanoparticles create 6 bands. Five of these bands lie below the Fermi level, which are denoted as d bands and 6th band, the last band which lie above the Fermi level is known as conduction band or sp band. In this sp band, there lies a lowest unoccupied molecular orbital (LUMO) and a highest occupied orbital (HOMO) [34–36]. In copper nanoparticle capped by linoleic acid, an excitation at 250 nm from Xenon laser lead to the excitation of d-band electrons into sp-conduction band. A radiative recombination of electron hole pair between d-band and sp-conduction band produces luminescence [18, 19, 30, 37–40], which occurs practically at 450 nm. This high energy band is due to radiative interband transition. In addition to this, a low energy band centered on 625 nm is observed, which can be attributed to the intraband transition between the HOMO-LUMO gaps [34]. It is found that the range for excitation wavelength to induce HOMO-LUMO transition at 625 nm is 240–270 nm. But the intensity is found out to be maximum when the sample is excited with 250 nm of an optical source. Moreover, the absorbed linoleic acid during the formation of copper nanoparticles further enhances the intensity of emission [37–40]. Flourescence spectra for copper nano-particle are shown in Fig. 6 which was performed on Hitachi; F-2500 model. It has been observed that with increase in concentration, intensity of the two emission peaks does not increase significantly. It has also been observed that both the UV–vis spectra and fluorescence

spectra do not show any change in their peak position up to 20 days or so, but after this period both the spectra do not replicate the spectra exactly and further some kind of agglomeration has been observed in TEM image of the sample. Hence we conclude that the sample starts to deteriorate after 20 days.

Summary

Linoleic acid capped copper nanoparticles have been prepared through the reduction of cupric ions by ethanol. XRD analysis and TEM image reveal that the prepared nanoparticles are spherical in shape with an average size of 5 nm, whereas FTIR spectra confirm the capping of copper nanoparticles by linoleic acid. These copper nanoparticles dispersed in chloroform show an absorption peak at 241 nm whereas two emission peaks are obtained at 450 nm and 625 nm in the fluorescence spectra corresponding to high and low energy band respectively, when excited with 250 nm of an optical source. All the analysis shows that these linoleic acid capped copper nanoparticles remain stable for 20 days.

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