Characterization of Kondagogu Stabilized Copper Nanoparticles and Their Surface Enhanced Raman Scattering Studies

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Received 31 March 2014; accepted 29 April 2014

Abstract

Novel green chemical reduction method was adapted to the preparation of copper nanoparticles using the natural stabilizer Kondagogu (Cochlospermum Gossypium). The Copper nanoparticles prepared were FCC crystalline with an average size of 20 nm and were stable in air for about 25 days. The UV absorption peak observed at around 558 nm was attributed to the absorption of copper nanoparticles. The FTIR spectrum analysis confirmed the presence of functional groups of stabilizer Kondagogu in capping the copper nanoparticles. The prepared copper nanoparticles were used to prepare substrates for surface enhanced Raman scattering (SERS) studies. The results showed that the prepared copper nanoparticle substrates exhibit strong surface enhanced Raman scattering (SERS) signal. The gum Kondagogu was proved to be an efficient stabilizer to the preparation of copper nanoparticles.

Key words: Chemical reduction, Copper nanoparticles, Green synthesis, Kondagogu, SERS

1. INTRODUCTION

Natural gums are of great interest owing to their wide applications as binders, emulsifiers and stabilizers. Low cost and ready availability are the main advantages of plant gums. Gum Kondagogu is a natural plant gum found in the exudate from the tree Cochlospermum Gossypium and it is the proved stabilizer. It belongs to the family Bixaceae and it has some characteristic properties such as high molecular weight, hydrogel property, high uronic acid content and high water binding capacity. Gum Kondagogu is slightly acidic in nature. Green synthesis of nanoparticles involves either reduction or oxidation as main reaction. Synthesis of metal nanoparticles using natural products is an economic and valid alternative for the large-scale production. Copper nanoparticles are preferred over other class of nanoparticles, because of their catalytic and optical properties. Various synthesis techniques have been employed to control the properties of nanomaterials such as size and shape. Chemical reduction is the preferred method over all other methods as it is simple and economical. The chemical reduction methods using different reducing and stabilizing agents are known to generate copper nanoparticles with controlled size and shape. The chemical reduction of metal salt in aqueous solution and precipitation of the nanoparticles is a novel approach. It was reported that the two stage chemical reduction process is necessary to avoid formation of copper oxide [1-8].

Noble metal nanoparticles have surface plasmons in the visible range of the electromagnetic spectrum enabling them to be used as SERS substrates. These form the backbone for SERS studies and have been synthesized in different ways and widely reported. The prime objective of SERS community is to develop substrates that are reproducible, cost effective, easy to prepare and environmentally benign. Present work is thus concerned with one-pot synthesis of copper nanoparticles via green chemical reduction route using natural stabilizer Kondagogu. Useful chemical strategies based on this synthesis have been established. This method allowed the environmentally friendly reaction conditions to obtain copper nanoparticles. The prepared green copper nanoparticles are used to develop SERS substrates and SERS studies on R6G have been demonstrated [9-11].

2. EXPERIMENTAL

2.1. Materials

The starting chemicals used for the preparation of copper nanoparticles are copper chloride, copper sulphate, L-Ascorbic acid, NaOH and Hydrazine Hydrate (HH). All chemicals used were of analytical reagent grade. The solutions were made with Millipore water. The natural extract gum Kondagogu was used as stabilizer.
2.2. Synthesis of copper nanoparticles

In the present study, copper nanoparticles were synthesized by chemical reduction method. Copper salts were used as basic precursors, Kondagogu as a stabilizer, HH as a reducing agent and L-Ascorbic acid as an anti-oxidant agent. NaOH was used as a catalyst and also to adjust the PH to 12. The gum Kondagogu solution of concentration 0.6 % w/v was prepared in Millipore water. The Copper chloride (0.04M) and L-Ascorbic acid (0.001M) solutions were prepared separately using Millipore water. The solutions of gum Kondagogu and L-Ascorbic acid were added to copper chloride solution under stirring. Then the solutions of HH (1M) and NaOH (0.01M) were added to the mixed copper salt solution under stirring. The initial blue color of the reaction mixture eventually turned to brown-black color. Stirring was continued for another 1 hr. to complete the reaction. The precipitate was washed twice with methanol after filtration and then dried to obtain copper nanoparticles. Similar procedure was adopted for copper sulphate.

2.3. Stabilization of copper nanoparticles

Water soluble polymers behave as stabilizers by raising the viscosity of the bulk phase. Consequently, the particles contain lower kinetic energy and the collisions become reduced. But, it was reported that the emulsion prepared with the water soluble polymer gum Kondagogu showed typical change in particle size and a high rate of coalescence. But, at higher gum Kondagogu concentrations, gelation and high viscosity were observed because of the increase in surface and interfacial tensions. This was because of the high content of acetyl groups (−COOCH3) present in the gum Kondagogu that imparts an amphipathic character to the molecule. The acetyl groups (hydrophobic) of the gum Kondagogu get adsorbed on the oil surface leaving hydrophilic (−OH) segments in the aqueous phase. 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 gum Kondagogu was used to prevent Cu cluster from aggregation. The mechanism of copper nanoparticles formation was shown in Fig. 1.

2.4. Characterization

Morphology and size of copper nanoparticles were investigated using Scanning Electron microscope (SEM-Hitachi S-3400N equipment) and Transmission Electron Microscope (EM-Phillips equipment). SAXS data were collected using Panalytical X-ray Generator (PW 3830) having SAXS 896986 Anton Paar mounted on it. The green synthesized copper nanoparticles were studied by UV-visible spectrometer (Lab India Instruments Pvt. Ltd, Lab India UV- 3000+). All spectra were corrected against the background spectrum of water as reference. The diluted sol was taken in the capillary sample holder and placed in the X-ray apparatus. XRD patterns of copper nanoparticles were recorded using Philips X-ray X-ray diffractometer coupled with graphite monochrometer. The scanning was done in the Bragg’s angle region (2θ) from 0° to 80° at a speed of 0.25° per minute using Cu Kα radiation. Crystal size was calculated using Williamson – Hall equation given as following.

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

(1)

where \( \lambda \) is wavelength of X-rays, \( \beta_{\text{hkl}} \) is the full width at half maximum of X-ray profile, D is the diameter or crystallite size of the particle, \( \varepsilon \) is the lattice strain and \( \theta \) is the Bragg angle. The FTIR spectra of copper nanoparticles were recorded by KBr pellet method using FTIR spectrometer (Bruker Optics, Germany, Tensor 27). SERS spectra were observed by micro-Raman spectrophotometer (Horiba LabRam HR 800 model).

2.5. Surface Enhanced Raman Scattering (SERS) substrate preparation

The gum Kondagogu stabilized copper nanoparticles prepared using different copper salts (copper chloride, copper sulphate) were used to prepare SERS substrates. The well characterized Rohdamine 6G (R6G) was used as a test analyte [12-13]. In the present study, SERS substrate was prepared by dropping copper nanoparticles on a glass slide. Rohdamine 6G (R6G) solution of 10^{-5} M concentration in ethanol was used as a test analyte to study SERS spectrum. A few droplets of the analyte solution were dropped and left to be dried on the SERS substrate. R6G molecules were adsorbed onto the metal nanoparticles of the SERS substrate after few minutes. Thus two SERS substrates were prepared.

3. RESULTS AND DISCUSSIONS

SEM images of the gum Kondagogu stabilized copper nanoparticles prepared from two different copper salts (copper chloride, copper sulphate) were shown in Fig. 2 (a-b). Copper nanoparticles by this method showed the monodispersed distribution of particle sizes with an average particle size around 25 nm. The composition of copper nanoparticles prepared was further probed by Energy-Dispersive X-ray (EDX) analysis. EDX spectra of prepared copper nanoparticles exhibited the peaks of copper nanoparticles as shown in Fig. 3 (a-b). In addition to this, a minute peak of oxygen was also observed. This indicated the presence of the little amount of copper oxide.

TEM images of the gum Kondagogu stabilized copper nanoparticles synthesized using two different copper salts (copper chloride, copper sulphate) were shown.
in Fig. 4 (a-b). The samples studied revealed the monodispersity of copper nanoparticles with an average particle size 20 nm. These results were also in agreement with SEM experiment results.

SAXS measurements were performed using Mo and Cr radiations with three different configurations to cover the wide q-range. Fig. 5 shows two SAXS intensity profiles of samples prepared using copper chloride (B2, circles) and copper sulphate (C2, diamond) along with the stabilizer Kondagogu. SAXS profiles were fitted with diluted spherical model and log-normal size distribution. Size distribution curves with the diameter are shown in the inset to figure. Mean particle size and Standard deviation are estimated and is given below.

B2: 1.54 nm & 0.39
C2: 1.71 nm & 0.42
Fig. 5: SAXS image of copper nanoparticles prepared from (a) copper chloride (c) copper sulphate

UV-visible absorption spectra of the gum Kondagogu stabilized copper nanoparticles prepared from two different copper salts (copper chloride, copper sulphate) were shown in Fig. 6. The copper nanoparticles prepared displayed an absorption peak at around 558 nm. This peak was assigned to the absorption of copper nanoparticles. The broadness of the absorption peak was attributed to the size distribution of nanoparticles. This result was also in agreement with SEM and TEM observations. Based on SEM, TEM and UV observations, it was conformed that prepared particles are copper nanoparticles. Since, no other measurable peak was observed in the spectrum that confirms that the synthesized products are Cu only.

Fig. 6: UV visible absorption spectra of copper nanoparticles prepared from (a) copper chloride (b) copper sulphate

X-ray diffraction patterns of the gum Kondagogu stabilized copper nanoparticles synthesized from two different copper salts (copper chloride, copper sulphate) were shown in Fig. 7. Three main characteristic diffraction peaks for Cu were observed at around 2θ = 43°, 50°, 74° correspond to (111), (200), (220) crystallographic planes of face-centered cubic (FCC) copper crystals (JCPDS No.04-0784). A small peak observed at around 62° indicates the formation of small amount of copper oxide. The lattice parameter ‘a’ has been calculated by using these profiles. The average value of the lattice parameters was found to be in agreement with reported value 3.615 Å in literature [14]. Crystallite size of copper nanoparticles was calculated using the equation (1), and found to be the average particle size around 5 nm.

Table 1 report the summary of the mean particle sizes determined from SEM, TEM, SAXS and XRD experimental methods. From the summary, it appears that the apparent, morphologically distinct copper nanoparticle size is on the order of nanometers, ranging from roughly 2 to 20 nm. This is consistent with previous analyses of the powders [15]. It may be noted that SEM and TEM revealed a fine structure within the particles. Both XRD and SAXS measurements, supported by TEM observations, resulted in a smaller particle size. This is most likely a measure of the crystal size within the particles. However, the SAXS with its greater resolution was able to identify at least two modes of crystallites within the sample.

Table 1. Summary of Methods and Results

<table>
<thead>
<tr>
<th>Method</th>
<th>Average Particle Size (nm)</th>
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<tbody>
<tr>
<td>SEM</td>
<td>20</td>
</tr>
<tr>
<td>TEM</td>
<td>20</td>
</tr>
<tr>
<td>SAXS</td>
<td>2</td>
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<td>XRD</td>
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Fig. 7: XRD patterns of copper nanoparticles prepared from (a) copper chloride (b) copper sulphate
The FTIR spectrum of copper nanoparticles exhibits several bands characteristic of stretching and bending vibrations of O-H, C=C and C-O functional groups. FTIR measurement was carried out to identify the possible molecules responsible for capping agent for the copper nanoparticles synthesized using Kondagogu stabilizer. FTIR spectra of the gum Kondagogu stabilized copper nanoparticles synthesized using different copper salts (copper chloride, copper sulphate) were shown in Fig. 8. The broad band observed at around 3450 cm⁻¹ and 617 cm⁻¹ illustrates the stretching frequency of hydroxyl group (O-H group) present in the surface of the copper nanoparticle. The band observed at around 1622 cm⁻¹ illustrates the bending vibrations of O-H bonds in OH groups. FTIR spectrum of pure Kondagogu contains peaks in the range of 650-1000 cm⁻¹, which are attributed to C-H bending vibrations. It is clear from Fig. 8 that these peaks in the range 650-1000 cm⁻¹ are shifted slightly to a higher wave numbers. These differences indicate that the thin Kondagogu layer have taken place on the surface of copper nanoparticle.

**Fig. 8:** FTIR spectra of copper nanoparticles prepared from (a) copper chloride (b) copper sulphate

The copper nanoparticles stabilized by gum Kondagogu stabilizer are stable for about 25 days and have shown no contamination during this period. However, the Kondagogu stabilizer layer on the surface of copper nanoparticle will be removed when they are washed in hot water. The copper nanoparticles washed in hot water have shown the contamination with copper oxide after few days. This observation confirmed that the Kondagogu molecules on the surface of copper nanoparticles are important to avoid oxidation. Also, as Kondagogu layer surrounded the copper nanoparticle, these prepared copper nanoparticles are useful in medical area. By selecting suitable reaction conditions, the present synthesis route has been demonstrated for the production of copper nanoparticles with an average particle size of 20 nm.

SERS studies on substrates prepared using ethanol soluble dye, R6G with Kondagogu stabilized copper nanoparticles were carried out and shown in Fig. 9. The gum Kondagogu stabilized copper nanoparticles prepared from copper chloride and copper sulphate were used to prepare two SERS substrates. The 1307 cm⁻¹ that corresponds to symmetric nitro stretch was the marker peak. This peak along with baseline correction was used to calculate the Surface Enhancement Factor (SEF). For 514.25 nm, SEF was evaluated as 7.7x10⁵. This enhancement can be attributed to the chemical SERS effect related to charge transfer between the copper nanoparticles and R6G. Strong peaks were observed at around 1368, 1514 and 1648 cm⁻¹ that correspond to the C-C stretch. The peak centered at around 612 cm⁻¹ corresponds to the C–C deformation in-plane vibration. On the other hand, the peak at around 780 cm⁻¹ was assigned to the C–H deformation out-of-plane vibration and the peak at around 1189 cm⁻¹ was assigned to the C–H deformation in-plane vibration. These wave numbers are observed to be deviated slightly compared to that of the normal Raman spectrum of R6G [12-13]. This deviation can be attributed to the slight change in the secondary structure of R6G, because of the interactions between R6G molecules and copper nanoparticles. Surface enhancement effect of copper nanoparticles was found to be good, but small.

**Fig. 9:** SERS spectra of substrates prepared using R6G with copper nanoparticles prepared from (a) copper chloride (b) copper sulphate

**CONCLUSIONS**

The gum Kondagogu stabilized copper nanoparticles were prepared using a simple green chemical reduction approach. The copper nanoparticles were stable in air for about 25 days. The average particle size was found be around 20 nm. The Raman signal was greatly enhanced by the SERS substrates prepared using the Kondagogu stabilized copper nanoparticles. The Raman enhancement effect of copper nanoparticles was found to be good, but small.

**ACKNOWLEDGEMENTS**

The authors thank Director, DMRL, Hyderabad and CFRD (Central facilities for Research and Development), Osmania University, Hyderabad for providing experimental facilities. The authors also thank Prof. A.K. Bhatnagar, School of Physics, HCU, Hyderabad for providing SERS facility. The authors are also grateful to the Head, Department of Physics, Osmania University, Hyderabad for the needful assistance.

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Source of support: Nil; Conflict of interest: None declared