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Honey mediated green synthesis of gold nanoparticles

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ABSTRACT

Bio-directed synthesis of nanoparticles is of interest to biologists, chemists and materials scientists alike, especially in light of efforts to find greener methods of inorganic material synthesis. Though the biosynthesis of gold nanoparticles has been carried out by several groups of scientists using plants, fungi and bacteria, so far there is no report on the use of natural honey – mankind's only sweetener for centuries – for the synthesis of nanoparticles. Here, it is a report on a greener synthesis of Au nanoparticles using honey as reducing and capping agents. By adjusting the concentrations of $HAuCl_4$ and honey in aqueous solutions, colloids having a larger propensity of either anisotropic or spherical nanocrystals could be obtained at room temperature. The nanoparticles obtained were characterized by UV–visible spectra, high-resolution TEM and XRD. The spherical particles obtained have a size ~15 nm as shown by XRD pattern and TEM image. The high crystallinity with fcc phase is evidenced by bright circular spots in SAED pattern and clear lattice fringes in the high-resolution TEM image. FTIR measurements were carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the Au nanoparticles synthesized using honey. The carboxylic acid group vibrations and amide I and II bands indicate the binding of protein with Au surface through the amine group rather than the carboxyl group.

1. Introduction

Gold nanoparticles have been considered important area of research due to their unique and tunable surface plasmon resonance (SPR) and their applications in biomedical science including drug delivery, tissue/tumor imaging, photothermal therapy and immunochromatographic identification of pathogens in clinical specimens [1]. Eco-friendly and cost-effective procedures for the synthesis of nanoparticles are of interest to biologists, chemists and materials scientists alike, especially in light of efforts to find "greener" methods of inorganic material synthesis [2]. The work reported all over the world on the role of microorganisms and plants in the synthesis of nanoparticles has been reviewed by Mohanpuria et al. [3]. Coriander leaf mediated synthesis of Au nanoparticles has been carried out by Narayanan and Sakthivel [4] very recently and the reduction of $AuCl_4^-$ is reported to be complete in 12 h. However, there is no report on the synthesis of nanoparticles using natural honey – the food of Gods – which was mankind's only sweetener for centuries. Honey is one of the world's healthiest foods and the major constituents are fructose and glucose and it contains aminoacids that help build up Ca in the body. Honey has been subjected to extensive study [5–9] all over the world on its ingredients, physicochemical properties, vitamins, mineral content and quality control. It is reported to benefit human longevity due to its high-energy, presence of chemical elements, vitamins and enzymes. Honey is rich in vitamin C and the important minerals present are K and Mg. Also, it contains ingredients that can function as anti-oxidants which play a vital role in the prevention of cancer. It is very interesting to know that in Kerala, the southern part of India, the great grandmas gave two–three drops of a mull made of honey and gold to new born babies thinking that gold supports longevity and memory. Interestingly, *saraswatharishtam*, an Ayurvedic medicine (based on the traditional Indian medical system), contains gold nanoparticles [10]. Here, it is a report on a "greener" synthesis method for the preparation of Au nanoparticles in water using natural honey. The term "greener" is used since natural honey is used as such for the synthesis and it acts as both reducing and protecting agents. Further, the synthesis is carried out at room temperature.

2. Experimental

Natural honey procured from Kerala Agriculture University and $HAuCl_4 \cdot 3H_2O$ (Sigma–Aldrich) were used as such. 50 mg of $HAuCl_4$ was dissolved in 120 mL deionized water. 20 g of honey was diluted to 70 mL. 10 mL of this aqueous solution of honey was added to 30 mL of $HAuCl_4$ and stirred well. The complete reduction of $AuCl_4^-$ is evidenced by light purple colour of the solution after 3 h giving colloid (g_1). The addition of honey was varied as 15, 20 and 25 mL to obtain colloids (g_2), (g_3), and (g_4), respectively. The speed of reduction is found to increase with increase in the addition of honey and

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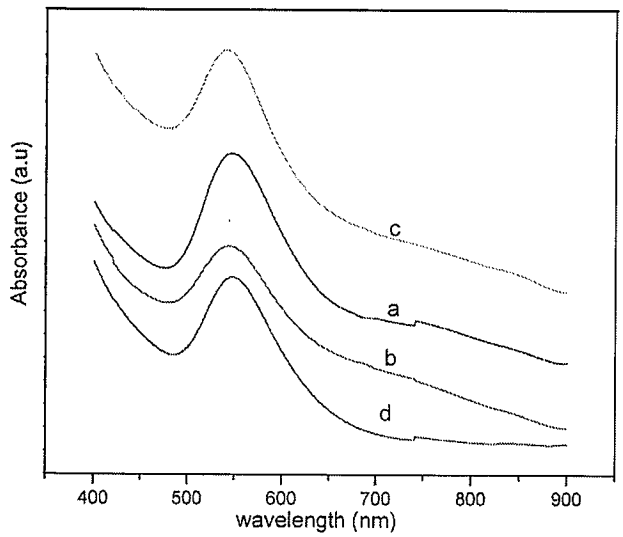

Fig. 1. UV–visible spectra of gold colloids: (a) g_1; (b) g_2; (c) g_3 and (d) g_4.

colloid (g_4) is obtained within 30 min. The final pH of the colloids was 3. A slight increase of pH could also speed up the reduction and was complete within a few minutes.

The UV–visible spectra were recorded on a Jasco V-550 UV–visible Spectrophotometer with samples in quartz cuvette. The photoluminescence (PL) spectra were obtained on a Flurolog III spectroflurophotometer with samples placed in non-fluorescent quartz cuvette. The excitation wavelength used was 300 nm. X-ray diffraction pattern of dry nanoparticle powder was obtained using Siemens D5005 X-ray diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm). The FTIR spectra were obtained on a Bruker IFS 100v instrument with the sample as KBr pellets. The morphology of the nanoparticles was analyzed using the high-resolution image obtained with a JEOL 3010 transmission electron microscope.

3. Results and discussion

The primary ingredient of honey is fructose, a monosaccharide and reducing agent. Also, it contains vitamin C, a slow reducing agent. Further, when honey is diluted with water, chemical reaction between glucose, water and oxygen produces small amounts of H_2O_2 and gluconic acid. This slow release of H_2O_2 makes honey a mild antiseptic. The acidity of honey reduces the number of organisms that can live in it. As glucose is changed to gluconic acid due to dilution with water, the presence of the reducing agent fructose in honey may be responsible for reduction. It is also possible that sucrose and proteins/enzymes play a role in the reduction. However, the ingredient responsible for the reduction of the chloroaurate ion needs further study.

3.1. UV–visible and TEM studies

Fig. 1 shows the UV–visible spectra of gold colloids (g_1)–(g_4) after 3 h of reaction. At lower concentrations of honey the SPR peak is broad with an absorption tail in the longer wavelength that extends well into the near infrared region attributing the excitation of the in-plane SPR which indicates significant anisotropy in the shape of Au nanoparticles. As the quantity of honey is increased the SPR goes on damping rapidly on the longer wavelength side and finally in colloid (g_4) a sharper absorption peak at 541 nm is observed which is characteristic of spherical particles. The typical TEM images obtained for colloids (g_1) and (g_4) are shown in Fig. 2.

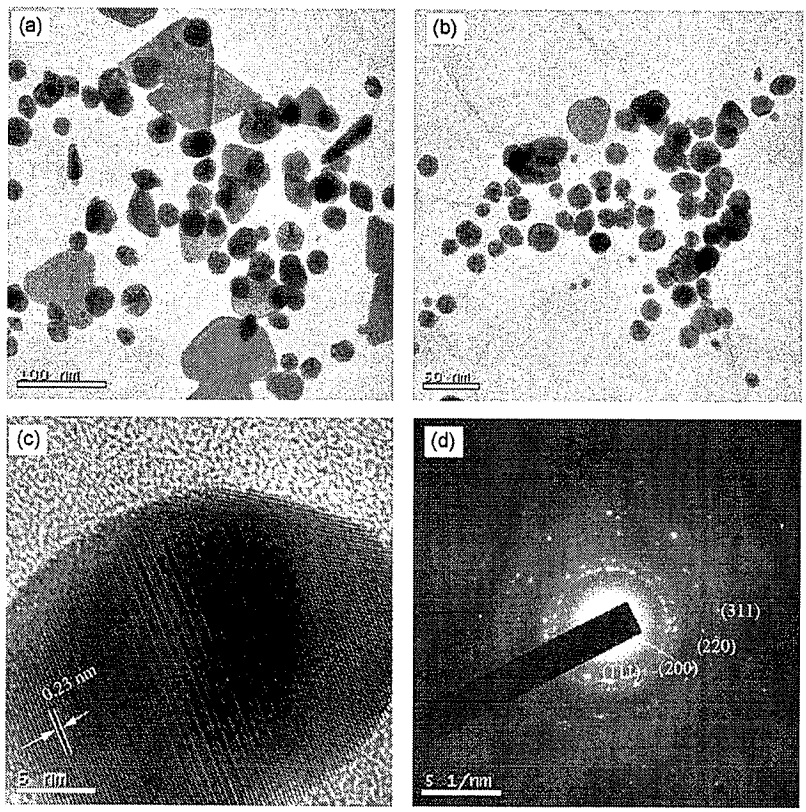

Fig. 2. TEM images of colloids: (a) g_1; (b) g_4; (c) high-resolution image and (d) SAED pattern.

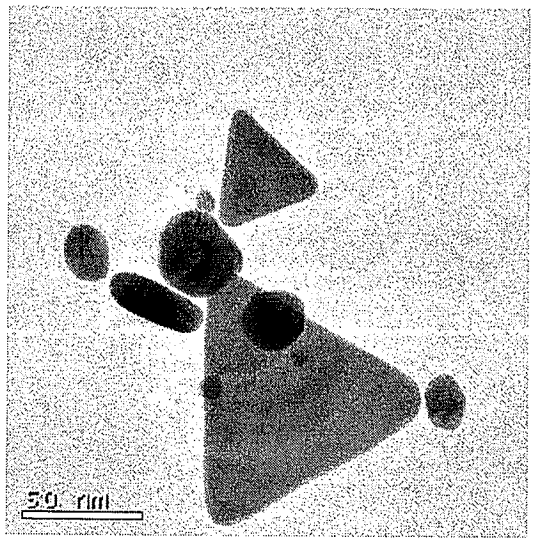

Fig. 3. Gold nanotriangle in colloid g_1 showing adherence of smaller particles.

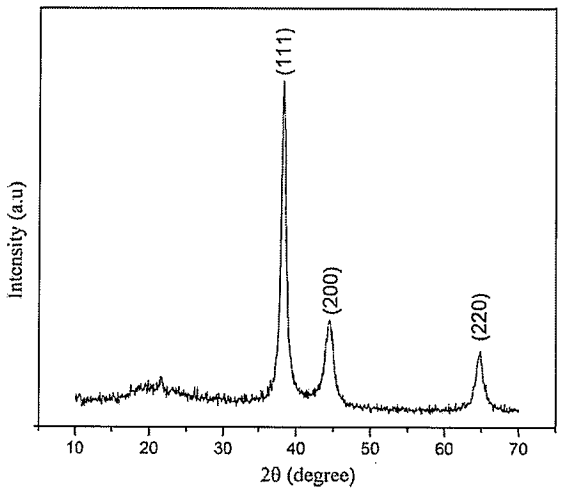

Fig. 4. XRD pattern of Au nanoparticles obtained using honey.

The decrease in anisotropy and particle size with increase in the quantity of honey is evident from the images. Colloid (g_1) consists of a larger propensity of triangular nanoparticles (Fig. 2a) when compared with those in the TEM image of colloid (g_4) shown in Fig. 2(b). Colloid (g_4) consists of almost spherical nanoparticles with average size ~15 nm. The typical high-resolution image (Fig. 2c) with clear lattice fringes having a spacing of 0.24 nm reveals that the growth of Au nanoparticles occurs preferentially on the (1 1 1) plane. The inter-planar distance of the Au (1 1 1) plane is in agreement [11] with the (1 1 1) *d*-spacing of bulk Au (0.2355 nm). The clear lattice fringes in high-resolution image and typical selected area electron diffraction (SAED) pattern (Fig. 2d) with bright circular rings corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes show that the nanoparticles obtained are highly crystalline.

When an excess of honey was used (in colloid g_4) to reduce the aqueous $HAuCl_4$, the biomolecules acting as capping agents strongly shaped spherical nanoparticles rather than nanotriangles though the reductive biomolecules were enhanced. Although lower quantities of honey (in colloid g_1) fulfilled the reduction of chloroaurate ions, they failed to protect most of the quasi-spherical nanoparticles from aggregating because of the deficiency of biomolecules to act as protecting agents. The nascent nanocrystals devoid of protection were unstable and gold nanotriangles might grow by a process involving rapid reduction, assembly and room temperature sintering of spherical gold nanoparticles [12]. Sintering of gold nanoparticles and their adherence to the nanotriangle in colloid (g_1) is evident from Fig. 3. The blunt angled nanotriangles in Fig. 2(a) is a result of the shrinking process arising from the minimization of surface energy [12]. The presence of large quantity of honey, causes strong interaction between protective biomolecules and surfaces of nanoparticles preventing nascent gold nanocrystals from sintering. With larger quantities of honey, the interaction is intensified, leading to size reduction of spherical nanoparticles.

3.2. XRD and FTIR studies

The crystalline nature of Au nanoparticles was confirmed from X-ray diffraction (XRD) analysis. Fig. 4 shows the XRD pattern of Au nanoparticles obtained using honey. The diffraction peaks appearing at 38.1°, 44.5° and 64.8° correspond to the (1 1 1), (2 0 0) and (2 2 0) facets [11–15] of the face centered cubic crystal structure, respectively. The peak corresponding to the (1 1 1) plane is more intense than the other planes. The ratio between the intensity of (2 0 0) and (1 1 1) diffraction peaks is much lower than the usual value (0.52) suggesting that the (1 1 1) plane is the predominant orientation [9]. The width of the (1 1 1) peak was employed to calculate the average crystallite size using Scherrer equation. It is found that the average size is ~15 nm which matches with the particle size obtained from TEM image of colloid (g_4).

The important ingredients of honey are fructose, glucose, sucrose, proteins, minerals and vitamins [5–9]. FTIR measurement was carried out to identify the possible biomolecules responsible for capping and efficient stabilization of Au nanoparticles synthesized using honey. Fig. 5 shows the FTIR spectrum of gold nanoparticles obtained in this study. Intense absorptions are observed at 1714, 1539 and 1043 cm^{-1}. The IR band at 1714 cm^{-1} is characteristic of the C=O stretching mode [11–13,15,16] of the carboxylic acid group. The band due to C–O stretching mode got merged in the very broad envelope centered around 1043 cm^{-1} arising from C–O–C symmetric stretching and C–O–H bending vibrations [17] of protein in honey. The amide I and II bands of proteins [18] are expected to occur as prominent IR bands around 1660 and 1535 cm^{-1}, respectively. In the present case, the intense band observed at 1539 cm^{-1} arises from the amide II band and the amide I band got merged in the intense band around 1714 cm^{-1}. Proteins can bind to Au nanoparticles through free amine groups or carboxylate ion of aminoacid residue in it [12,15,19]. The presence of C=O stretching mode indicates the presence of –COOH group in the material bound to Au nanoparticles. Thus, the bands at 1714 and 1043 cm^{-1} in IR indicate the possibility that Au nanoparticles are bound to proteins through free amine groups.

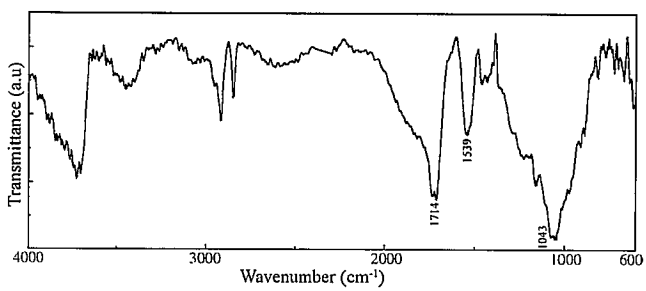

Fig. 5. FTIR spectrum of Au nanoparticles.

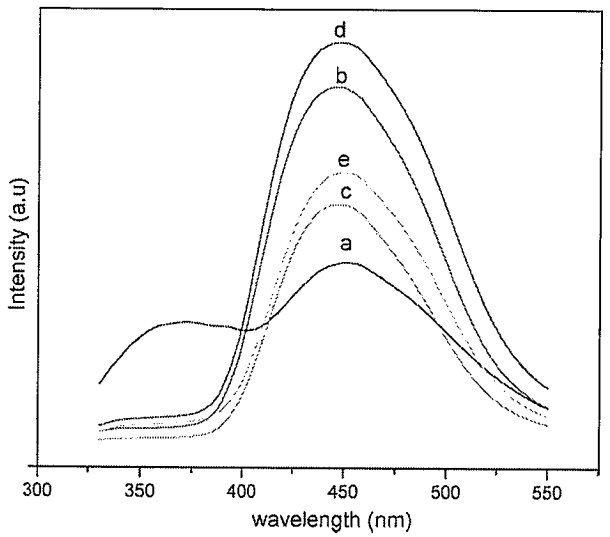

Fig. 6. PL emission spectra using an excitation of 300 nm (a) pure honey; Au colloids synthesized using honey (b) g_1; (c) g_2; (d) g_3 and (e) g_4.

3.3. Photoluminescence spectra

Nanosize metals like gold and silver have been reported [20–25] to exhibit visible photoluminescence (PL) arising from interband transitions. In the present case, all the synthesized Au nanoparticles are found to be photoluminescent. The PL spectra of gold nanoparticles at an excitation of 300 nm are shown in Fig. 6. Honey itself is luminescent (Fig. 6a). The PL band decreases in intensity from colloid (g_1) to (g_4). However, an enhancement in intensity with respect to pure honey is observed in all the colloids. This luminescence at 447 nm may be due to the funtionalization of Au nanoparticles with biomolecules in honey. Surface enhancement of fluorescence has been reported earlier in gold nanoparticles [10,26–29]. PL spectra with band around 522 nm were reported in biotin functionalized gold nanoparticles [30,31]. Gold nanoparticles synthesized using pseudomonas aeruginosa 1, 2 and 3 are also reported [32] to be photoluminescent with bands at 583, 571 and 591 nm, respectively. The PL emission indicates possible use in therapeutic applications. The position and shape of the PL band are independent of excitation wavelength indicating the absence of Raman bands in this region.

4. Conclusions

This honey-mediated biosynthesis of Au nanoparticles is greener than all the other reported methods. Also, the method has advantages like ease with the process can be scaled up and economic viability. There is increased productivity of Au nanoparticles compared to other biosynthesis routes already reported. The possible reducing agent is fructose and capping material responsible for stabilization is proteins present in honey. Visible PL emission around 447 nm indicates the possible use of the colloids in therapeutic applications.

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