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Green synthesis of silver nanoparticles using local honey

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Abstract. In this work, silver nanoparticles have been successfully prepared with a simple, cost-effective and reproducible aqueous room temperature “green” synthesis method. Honey was chosen as the eco-friendly reducing and stabilizing agent replacing most reported reducing agents such as hydrazine, sodium borohydride ($NaBH_4$) and dimethyl formamide (DMF) which are highly reactive chemicals but also pose a biological risk to the society and environment. The size and shape of silver nanoparticles were modulated by varying the honey concentration and pH of the aqueous solution that contain silver nitrate as the silver precursor, sodium hydroxide as the pH regulator and ethylene glycol as the solvent. The silver nanoparticles obtained are characterized by field- emission scanning electron microscope (FESEM), ultraviolet-visible spectra (UV-Vis) and Fourier transform infrared spectroscopy (FTIR). From SEM analysis, it was found that by increasing the concentration of honey, the size of silver nanoparticles produced decreased, from the range of 18.98 nm - 26.05 nm for 10 g of honey to 15.63 nm - 17.86 nm for 40 g of honey. Similarly, the particle size decreased as the pH of the aqueous solution increased. UV-Vis spectra revealed large anisotropic and polydispersed Ag nanoparticle were produced.

Introduction

In recent years, silver nanoparticles have attracted much attention due to its promising applications in many areas such as biological sensors, drug and gene delivery, antimicrobial protection, catalysis, electronics, energy storage and biomedical applications [1,2,3]. As a result, it has emerged as one of the noble metals that has been studied extensively [4]. Numerous reports on the synthesis of silver nanoparticles using diverse methods such as physical and chemical methods, electrochemical reduction, photochemical reduction and heat evaporation have been published [5]. Generally, hydrazine, sodium citrate and sodium borohydride are the most common chemical reducing agents extensively been used to produce metallic nanoparticles even though subjected to paramount concern. These toxic chemicals used to reduce the corresponding precursor salts to create uniform suspension however pose a biological risk to the society and environment [6]. Apart from the hazardous issues, some methods remain expensive such as lithography, laser ablation, aerosol technologies and ultraviolet irradiation. Therefore, there is a growing interest to develop a simple, clean, environmental-friendly, biocompatible, cost effective and sustainable methods to improve and/or protect our global environment [7]. Currently, efforts and initiatives to synthesis metallic nanoparticles of different compositions, sizes and controlled dispersity by green synthesis are ongoing rapidly and deserve merit. Ramanathan et al. [8] suggested that green synthesis of silver nanoparticles should involves three main steps, which must be evaluated based on green chemistry perspectives, including: selection of solvent medium, selection of environmentally benign reducing agent, and selection of nontoxic substances for the silver nanoparticles stability.

Recently, there a trend to search natural products with antibacterial, antioxidant and antitumor activity [9]. Many interesting biosynthesis methods are been employed under the name of green synthesis to produced nanosized silver nanoparticles from plant extracts including stem barks of Boswellia ovalifoliolata Bal. and Henry and Shorea tumbuggaia Roxb. [10], soap nuts [11], Cleome Viscosa leaf [12], Polyalthia longifolia leaf [13], Argemone Mexicana leaf [14], papaya fruit [15], Hibiscus rosa sintesis leaf [16] and Arbutus Unedo leaf [17]. Emanuela et al. [18] have reported a totally green approach toward rapid synthesis of silver nanoparticles using sucrose and maltose without using micro-wave irradiation or other intermediate steps. The used of fungi, algae and bacteria besides plant extract in the green synthesis of silver nanoparticles were reviewed by Krishnan and Kamala [19]. Vast development in green nanotechnology is significantly proven based on these literature studies.

Apart from the mentioned biotemplates used to synthesis silver nanoparticles, honey is another exceptional candidate yet to be fully explored by researchers around the world. Natural honey also contains many minerals and vitamins beneficial to man. It has extraordinary healing qualities e.g., antibacterial, anti-inflammatory and analgesic properties that go beyond it used as a food. In addition, honey also contains ingredients that are capable of preventing cancer due to its anti-oxidants properties [20]. The use of honey in the synthesis of silver nanoparticles in water has been reported recently [21]. However, the quality and composition of honey with respect to carbohydrates content such as fructose, glucose, sucrose and maltose depends on location. Similarly acidity level, water content, flavour and aroma, absence of defects, consistency and clarity, differ from one another based on its origin. Based on this premise, the work explored the used of local natural honey as reducing and capping agents to synthesis silver nanoparticles in aqueous at room temperature. The nanoparticles have been characterized by UV-Vis, FESEM-EDX and FTIR analysis.

Experimental

Local natural honey (Tualang) procured from wild forest of Malaysia and silver nitrate, $AgNO_3$ obtained from Bendosen chemicals were used as such. In a typical experiment, 20 g of honey was dissolved in 80 ml of deionized water. 15 mL of this honey was added to 20 mL aqueous solution of $AgNO_3$ (10^{-3} M) and stirred well for 1 min. To initiate the reduction of Ag ions, the pH was adjusted to 6.5 using NaOH. Reduction takes place rapidly as indicated by the golden yellow colour of the solution which gives colloid s_1. Colloids s_2, s_3, s_4 and s_5 are obtained by adjusting the pH of the solution to 7, 7.5, 8 and 8.5. Colloids s_6, s_7, s_8 and s_9 are obtained using different concentration of honey, 10 g, 20 g, 30 g and 40 g with a fixed pH value. These colloids are found to be stable for about 5 months without any stabilizing agent.

The UV-visible spectra were recorded on a Perkin Elmer Lambda 25 UV-vis spectrometer. The FTIR spectra were obtained on a Perkin Elmer Spectrum RX 1 FTIR spectrometer with resolution of 4.0 cm^{-1}. The morphology of the silver nanoparticles were analyzed using Zeiss Supra 35VP field-emission scanning electron microscope (FESEM).

Results and Discussion

SEM Studies. Reduction of silver (Ag) ions was observed to take- place with the addition of NaOH which acts as pH regulator. The morphology of silver nanoparticles obtained at different pH can be observed from SEM micrograph (Fig. 1). Based on the results, the particles size decreased as the pH of the aqueous solution increased. It can be deduced that there is a rapid reduction of Ag ions and formation of small nanoparticles at higher pH value. At pH of 7.5 the mean size obtained was 14.52 nm (Fig. 1(a)) and finally at pH of 8.53 the mean nanoparticles obtained was 11.16 nm (Fig. 1(b)) using the same concentration of honey which is 30 g.

Honey is an extremely complex food product that has been reported to contain at least 181 different substances including proteins, enzymes, amino acids, minerals, vitamins and polyphenols [20,21]. There is a possibility that sucrose, glucose and proteins/enzymes play a part in the reduction process. The addition of NaOH, which consequently increased the pH of the solution has an effect on the size of the nanoparticles produced. This probably due to the increased formation of gluconic acid from glucose as pH increased. Based on a number of literature studies, gluconic acid is formed from glucose because the base drive the opening of the glucose ring by abstraction of the α-proton of the sugar ring oxygen. The Ag ions then oxidized glucose to gluconic acid and itself reduced to metallic Ag.

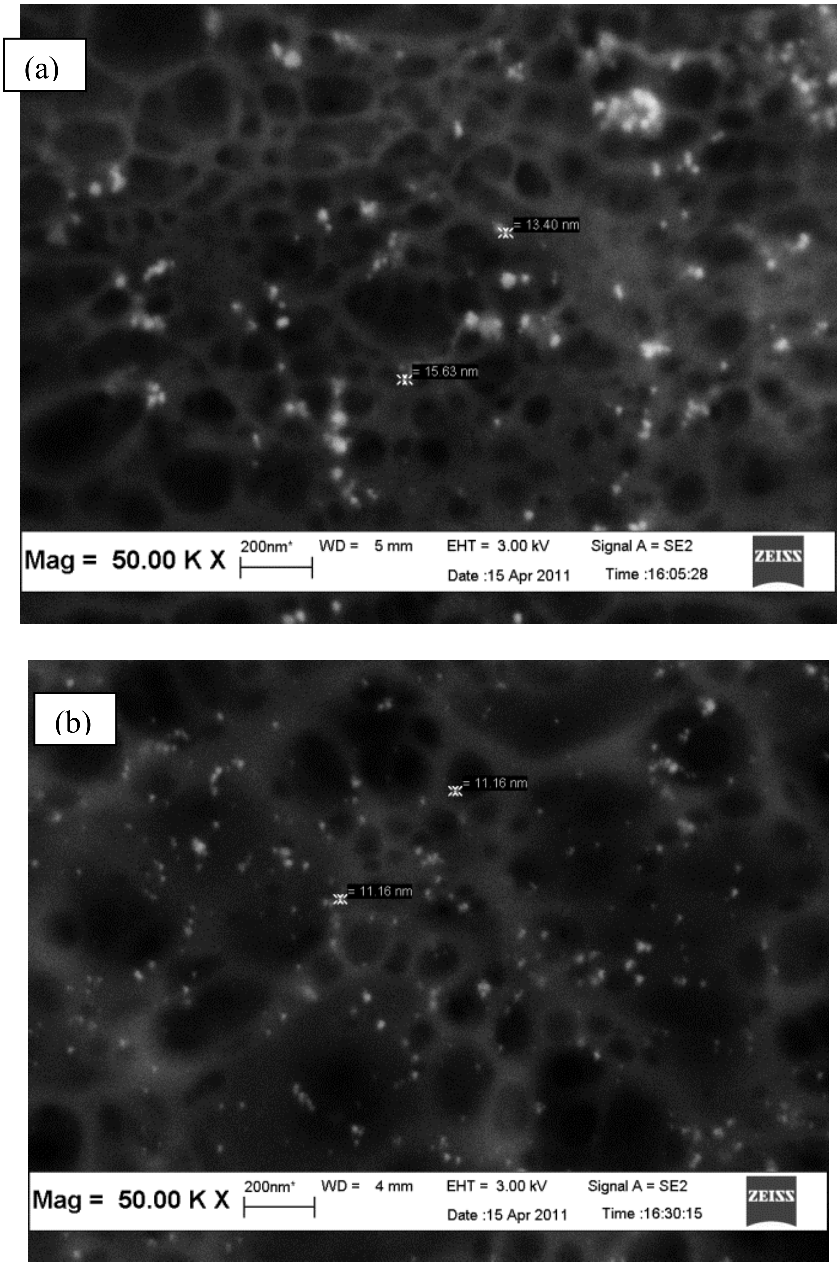

Fig. 1. SEM micrograph of silver nanoparticles (a) pH 7.5 (b) 8.53.

However the actual ingredient which is responsible for the reduction of the Ag ions still remains unknown and needs further study. Fig. 2 shows the SEM micrograph for the effects of different honey concentrations at a fixed pH value on the morphology of silver nanoparticles produced. The particle sizes obtained are between the range of 18.98 nm to 26.05 nm for 10 g honey, colloid s_6 (Fig. 2(a)) and between from the range of 15.63 nm to 17.86 nm for 40 g of honey, colloid s_9 (Fig. 2(b)). From these results, it can be said that honey concentrations have an effect on the particle size of silver nanoparticles produced. Higher amount of honey leads to size reduction of Ag ions compared to lower amount of honey in the aqueous solution. It is clearly evidence that honey contains components such as fructose, glucose, differemnt acids, vitamins and minerals that acts as the reducing as well as caping agents. There was a possibility that honey also contains other components namely sucrose and proteins/enzymes that can also contribute in the reduction of Ag ions however needs further study. The results are in strong agreement with the UV-Vis spectroscopic data discussed in the next section.

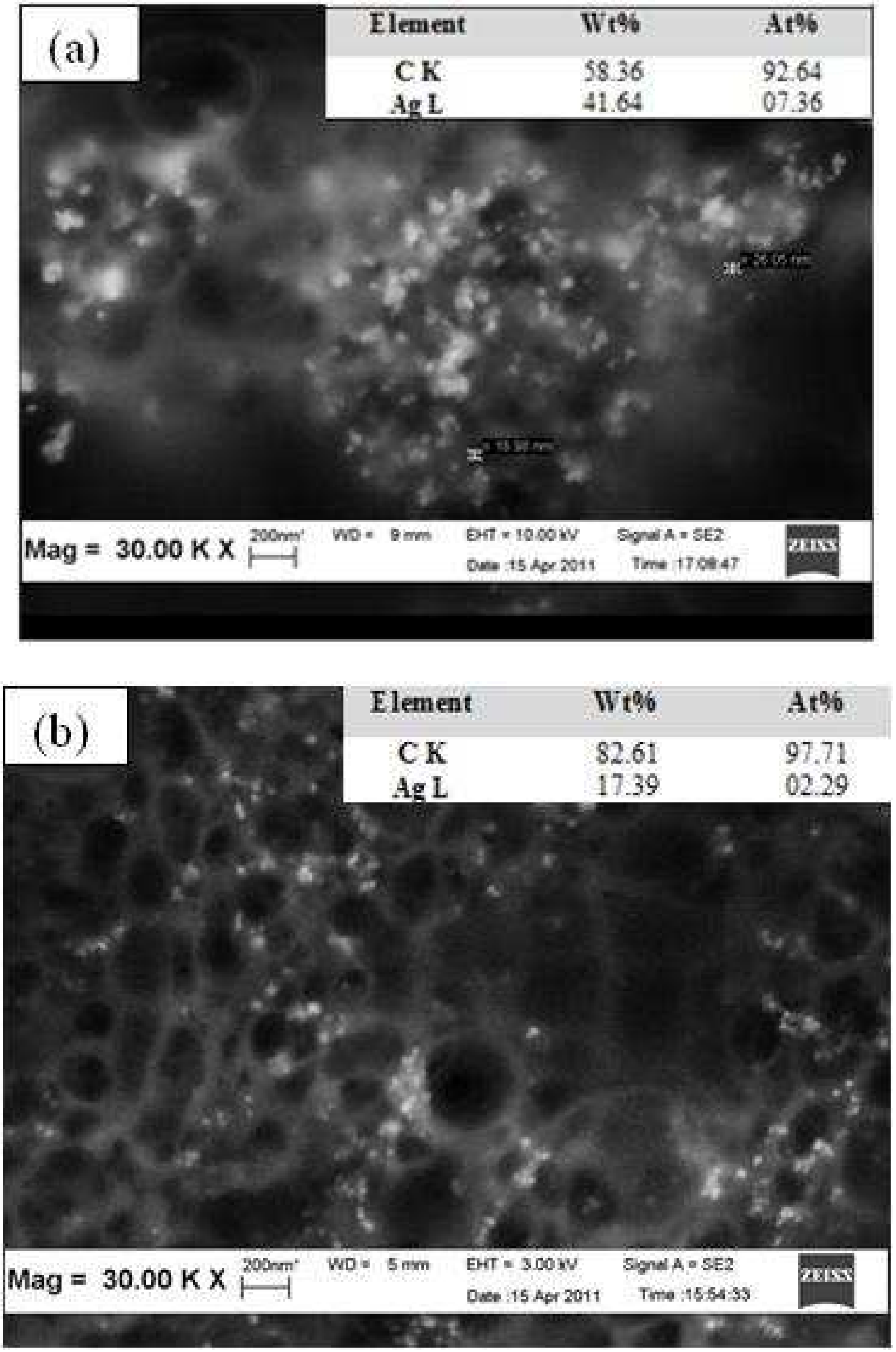

Fig. 2. SEM micrograph of silver nanoparticles (a) 10 g honey (b) 40 g honey.

UV-visible Studies. Fig. 3 shows the UV-Vis spectra for the various samples prepared at various pH. Generally the absorption spectra of the Ag nanoparticles produced exhibited a strong broad peak which shifted towards higher wavelength with increased pH. Broadening of the absorption peaks is indicative of formation large anisotropic and polydispersed nanoparticles. The surface plasmon resonance (SPR) appears at 490, 482, 430 and 424 nm for pH 6.67, 7.00, 7.51 and 8.01 respectively. The shifting of the absorption peaks towards higher wavelength with decreased in pH might be due to the increased in size of the Ag nanoparticles produced in this work. This finding correlate well with SEM results discussed earlier. The only anomaly in this trend is pH 8.65 whereby the absorption peak is higher than pH 7.51.

FTIR studies. FTIR measurements were carried out to identify the possible biomolecules responsible for capping and stabilization of the nanoparticles synthesized using honey. Fig 4. shows the FTIR spectrum of silver nanoparticles obtained in this study. Reduction of Ag ions takes place on addition of NaOH. The base facilitates the opening of the glucose ring by abstraction of the alpha-proton of the sugar ring oxygen and the metal ions oxidise glucose to gluconic. It is also possible that sucrose and protein/enzyme play a role in the reduction.

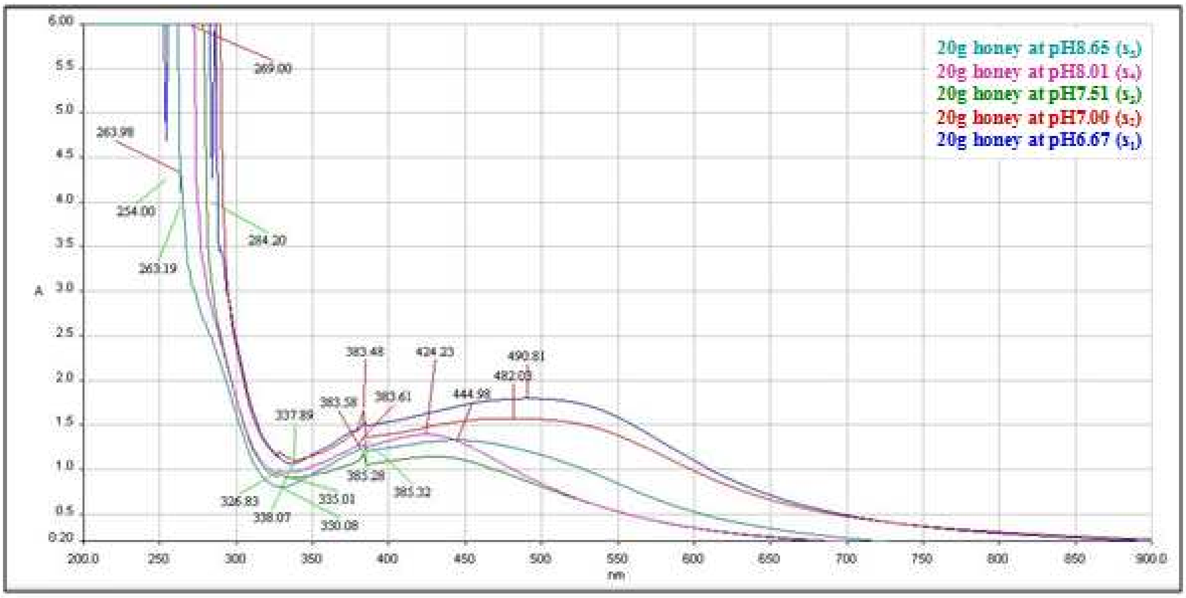

Fig. 3. UV-vis Spectra of silver colloids obtained at different pH values.

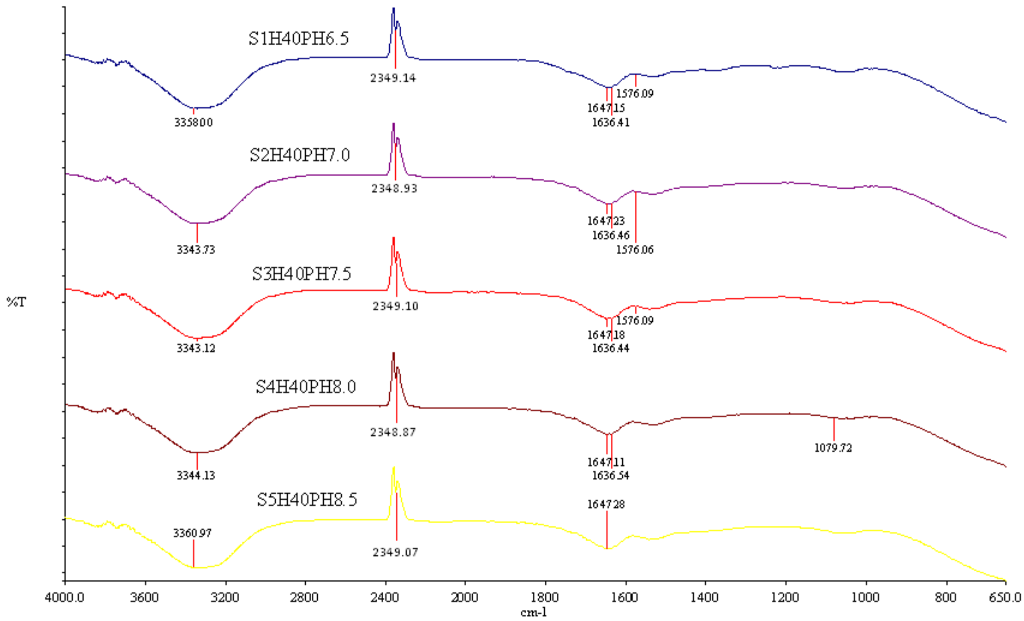

Fig. 4. FTIR spectrum of silver nanoparticles at difference pH values.

However the ingredient responsible for the reduction of the ions needs further study.. The amide I and II bands of protein are expected to occur as prominent IR bands around 1660 and 1535 cm^{-1}. In the present work, the bands are observed at 1647 and 1576 cm^{-1}. These bands are due to the carboxyl stretch and N-H deformation vibrations in the amide linkages of protein. Protein can bind to Ag nanoparticles through free amine group or carboxylate ion of the amino acid residue in it. The weak bond at 1079 arises from the C-O-C symmetric bending and C-O-H bending vibrations of protein in the honey. The observation of C-O stretch, amide I and II bands and the absence band due to the stretching mode of C=O in the IR spectrum of Ag nanoparticles indicates stabilisation of the system through the COO^- (carboxylate ions) groups of amino acid residues with free carboxylate groups in the protein.

Conclusion

The development of a reliable and eco-friendly process for the synthesis of metallic nanoparticles is critically needed in the field of nanotechnology. We have demonstrated that the use of honey, a natural, low cost reducing agent can produced Ag nanoparticles through green methodology thus avoiding the presence of hazardous and toxic solvent and waste. Silver nanoparticles of sized ~ 11.16 nm are synthesized at ambient conditions using $AgNO_3$ and honey at pH 8.53. The probable reducing agent is glucose while being stabilised by the protein present in the honey. This synthesis route has the advantage of being green and hence is eco-friendly.

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