RESEARCH ARTICLE

The Bio-fabrication of Gold Nanoparticles (AuNPs) by Green Method and Study of its Electrochemical Applications

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Abstract

This study reports a green method for the synthesis of gold nanoparticles (AuNPs) using the aqueous extract of *Salix aegyptiaca* extract. The effects of gold salt concentration, extract concentration and extract quantity were investigated on nanoparticles synthesis. Novel methods of ideally synthesizing AuNPs are thus thought that are formed at ambient temperatures, neutral pH, low costs and environmentally friendly fashion. AuNPs were characterized with different techniques such as UV-vis spectroscopy, FT-IR spectroscopy, X-ray diffraction, and TEM. FT-IR spectroscopy revealed that gold nanoparticles were functionalized with biomolecules that have primary carbonyl group, -OH groups and other stabilizing functional groups. TEM experiments showed that these nanoparticles are formed with various shapes and X-ray diffraction pattern showed high purity and face centered cubic structure of AuNPs. For electrochemical properties of AuNPs, a modified glassy carbon electrode using AuNPs (AuNPs/GCE) was investigated. The results show that electronic transmission rate between the modified electrode and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ increased.

Keywords: *Salix aegyptiaca*; Gold nanoparticles, biosynthesis, Electrochemistry

1. Introduction

Green processes with the use of economic, efficient and ecofriendly are gaining much importance due to the benefits associated with their use. Several plants have been studied for green synthesis of nanoparticles. The extracts of *Rosa damascena*, *Geranium*, *Emblica Officinalis* Lemongrass, *Chenopodium album* leaf and etc. have shown potential in reducing metals. In the present study, we report the synthesis of AuNPs by the reduction of gold ions using *Salix aegyptiaca* extract (1-6). *Salix aegyptiaca* (musk willow) is a *Salix* species that is cultivated in the Middle East and concoctions from the bark, leaves, and essence from the flowers are consumed widely as health drinks. The extracts of *Salix aegyptiaca* have potent antioxidant activity (7-14). Because many of these antioxidants also have potent anticancer properties, the ethanolic extract from the bark of *Salix aegyptiaca*, with the highest antioxidant and antiproliferative profile, was investigated for its effects on colorectal cancer. Catechol, catechin, and salicin were found to be the main constituents of the extract in addition to smaller amounts of gallic acid, epigallocatechin gallate (EGCG), quercetin, coumaric acid, rutin, syringic acid and vanillin (15-21).

Catechin is a flavan-3-ol, a type of natural phenol and antioxidant. It is a plant secondary metabolite. Catechin possesses two benzene rings and a dihydropyranheterocycle with a hydroxyl group on carbon 3. Electrochemical experiments show that catechin oxidation mechanism proceeds in sequential steps, related with the catechol and resorcinol groups and the oxidation is pH-dependent (22-27). The oxidation of the catechol 3',4'-dihydroxyl electron-donating groups occurs first, at very low positive potentials, and is a reversible reaction. The hydroxyl groups of the resorcinol moiety oxidized afterwards were shown to undergo an irreversible oxidation reaction. Salicin is an alcoholic β -glucoside. Salicin is produced in (and named after) willow (*Salix*) bark and acts as an anti-inflammatory agent in the human body. Salicin is also commonly found in the bark of *Populus* species, and the leaves of willows and poplars (1, 28-36). It is

also found in castoreum, which was used as an analgesic, anti-inflammatory, and antipyretic. Salicin hydrolyzes in the gastrointestinal tract to give D-glucose and salicyl alcohol. Upon absorption, salicyl alcohol is oxidized into salicylic acid and other salicylates compounds such as saligenin, salicyluric acid, salicyl glucuronides, and gentisinic acid which all are eliminated through the kidney. Catechol, also known as pyrocatechol is an organic compound with the molecular formula $\text{C}_6\text{H}_4(\text{OH})_2$. Small amounts of catechol occur naturally in fruits and vegetables, along with the enzyme polyphenol oxidase. The formation of the dianilinoquinone thus obtained is regarded by them as evidence that o-quinone is the initial oxidation product in the reaction. The proposed mechanism of oxidation of the major compound in the extract is shown in Figure 1.

Fig. 1. The proposed mechanism of oxidation of salicine, catechol, catechin in the process of reduction of gold ions

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2. Material and Method

Preparation of extract and synthesis of AuNPs

Flowers of *Salix aegyptiaca* were collected from Ghamsar Kashan, Iran, during the 2016 harvest season. The plant materials were identified morphologically at the herbarium of the Medicinal Plants Research Institute of Moor pharmaceutical. Then flowers washed with deionized water and dried. One gram of dried flower was added to 100 mL distilled water in a 150 mL Erlenmeyer flask. The extraction was done with a magnetic heater stirrer at 80 °C for 1 h. The solution was filtered and stored at 4 °C for further experiments. This solution was considered as 100% extract and other concentrations of the extract were prepared using this. Then different volume of *extract* was added to a vigorously stirred 30 mL aqueous solution of HAuCl_4 (1×10^{-3} M) and were sonicated with a 45 W 20 kHz ultrasonic pulse for 2 min.

3. Results and Discussion

XRD analysis

The XRD pattern (Fig. 2) shows that reflection peaks appeared at 38.4° , 44.6° , 64.8° and 77.6° which correspond to (111), (200), (220) and (311) miller indices, respectively. These are characteristic of fcc (face centered cubic) structure. The broadening of peaks confirmed the formation of nanoparticles. Scherrer equation was used for average particle size calculation and the size was found to be 16 nm. There is no additional peak in XRD pattern, which indicates high purity of GNPs.

FT-IR studies

FT-IR absorption spectra are shown in Figure 3. *Salix aegyptiaca* have been reported to consist of salicine, catechine, catechol as the major component. The IR bands observed at 1370 and 1740 in extract are characteristic of the C-O and C=O stretching modes of the carbonyl functional group in ketones, aldehydes, and carboxylic acids.

TEM analysis of nanoparticles

The TEM images (Fig. 4a) showed polydisperse nanoparticles with different shapes such as spherical, triangular and hexagonal. Average particle size was found to be 16 nm. The histogram size distribution graph is shown in figure 4b).

Fig. 2. XRD patterns of AuNPs synthesized by treating 30 mL HAuCl_4 1×10^{-3} M with 20 mL extract.

Fig. 3. FTIR spectra of (a) dried salix aegyptiaca extract (b) AuNPs

Fig. 4. (a) The TEM micrographs of AuNPs synthesized by 30 mL HAuCl_4 1×10^{-3} M with 20 mL salix aegyptiaca extract. (b) Histogram of the size distribution of AuNPs

UV-vis absorbance spectroscopy

It is well known that color transformation from light pink to deep red is the indication of AuNPs formation. These colors arise due to excitation of surface plasmon resonance (SPR) in the AuNPs. UV-vis

spectra of these aliquots were monitored as a function of time (Fig. 4. a, b). These biosynthesized AuNPs were laid aside at room temperature 6 months later.

Fig. 5. (a) UV-vis absorption spectrum of AuNPs at different *salix aegyptiaca* extracts quantity (30 mL HAuCl₄ 1×10^{-3} M with 8, 10, 12, 14, 16, 18 and 20 mL extract. (b) UV-vis absorption spectrum of AuNPs recorded as a function of reaction time with *salix aegyptiaca* extract.

Electrocatalytic activity of biosynthesized AuNPs

Electrocatalytic activity of green synthesis of AuNPs was measured by cyclic voltammetry (CV). After the self-assembly of AuNPs in glassy carbon electrode (GCE) an obvious increase in redox peak currents and decrease in peak-to-peak separation are observed. AuNPs assembled GCE electrodes was used for determination of polyphenols and flavonoids in traditional medicine formulations.

4. Conclusion

A simple and rapid synthesis based on the bio-reduction ability of the *salix aegyptiaca* has been developed to produce AuNPs. The major compound of extract act as a reductant as well as a capping material to protect the AuNPs surfaces and prevent the particles from aggregation, which has several advantages such as more surface availability and can function effectively. Also, it provides efficient, simple and good control over the synthesized AuNPs. Also, the TEM, UV-Vis, SEM, XRD and FT-IR of the composite were reviewed.

Declaration of Conflict of Interests

The authors declare that there is no conflict of interest.

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