This document is published in:

Materials Letters (2012). 76, 18-20.
DOI: http://dx.doi.org/10.1016/j.matlet.2012.02.025

Green synthesis and characterization of silver nanoparticles produced using *Arbutus Unedo* leaf extract

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Abstract: Metallic nanoparticles have received great attention from chemists, physicists, biologists and engineers who wish to use them for the development of a new generation of nanodevices. In the present study silver nano-particles were synthesized from aqueous silver nitrate through a simple and eco-friendly route using leaf broth of Arbutus unedo, which acted as a reductant and stabilizer simultaneously. The aqueous silver ions when exposed to the leaf broth were reduced and stabilized over long periods of time resulting in the green synthesis of surface functionalized silver nanoparticles. The bio-reduced silver nanoparticles were appropriately characterized. The results revealed the formation of single crystalline Ag nanoparticles with a nar-row size distribution for each sample. The particles, although discrete, were predominately coated with the organic leaf extract forming small aggregates, which makes them stable over long time periods and highly appropriate for coatings or biotechnology applications.

Keywords: Green synthesis, Silver nanoparticles, Organic coating

1. Introduction

In recent years nanomaterials fabrication and their uses is emerging as a critical technology with applications in many industrial sectors. Nanoparticles, due to their specific electrical, optical, magnetic, chemical and mechanical properties are currently used in many high technology areas, such as the medical sector for diagnosis, antimicrobial, drug delivery [1], as well as in the electronic and optoelectronic industry [2] or in the chemical sector for catalysis [3], for environmental protection [4] and energy conversion [5].

Nanoparticle synthesis is usually carried out by various physical and chemical methods, such as laser ablation, pyrolysis, chemical or physi-cal vapor deposition, sol gel, lithography electro-deposition most of them being expensive, and/or requiring the use of toxic solvents [6]

Recently, great efforts are made to use environmentally friendly methods for the synthesis of noble metal nanoparticles [7]. This is achieved mostly by the use of plant or fruit extracts [8] and bioorganisms [9]. These green methods are low cost, fast, efficient and generally lead to the formation of crystalline nanoparticles with a variety of shapes (spheres, rods, prisms, plates, needles, leafs or dendrites), with sizes between 1 and 100 nm. These features mainly depend on the process parameters, such as the nature of plant extract and the relative concentrations of the extract and metal salt(s) reacting, pH, temperature, and time of reaction, as well as the rate of mixing of plant extract and metal salt(s) [10]. The stability of produced nanoparticles can in some cases change after a few days or the nano-particles can remain stable over long periods [11].

In the present paper we present an environmentally friendly, one step, ultra-fast, cost-efficient method for producing Ag nanoparticles using readily available native Macedonian region Greek plant extracts. Some of the produced nanoparticles are covered by a stable organic coating, i.e. are surface functionalized, which makes them stable over long periods and also suitable for a variety of medical applications such as drug delivery.

This type of surface functionalization of metal nanoparticles has not been systematically reported for most if not all of the plant extracts previously used for the green synthesis of noble metal nanoparticles, and may constitute a unique phenomenon observed only with few specific plants.

2. Materials and methods

2.1. Preparation of Arbutus unedo leaf broth

Silver nitrate ($AgNO_3$) was purchased from Sigma-Aldrich chemicals and fresh Arbutus Unedo leaves were collected from surroundings of Thessaloniki region, Macedonia, Greece. The *Arbutus unedo*

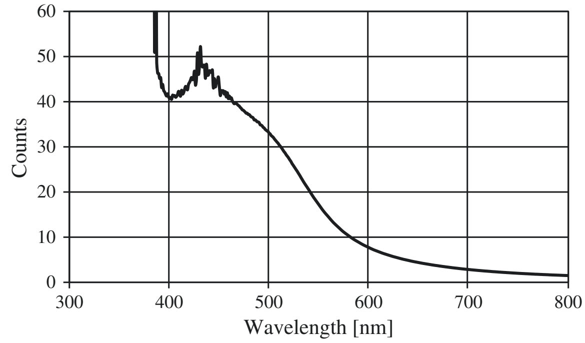

Fig. 1. The UV-absorption spectra obtained for *Arbutus unedo* plant. A characteristic peak at 450 nm wavelength is clearly observed, which is indicative of the formation of Ag nanoparticles.

fresh leaf extract used for the reduction of Ag^+ ions to Ag° was prepared by placing 10 g of thoroughly washed finely cut leaves in 500 ml flask along with 100 ml of distilled water and then boiling the mixture for 15 min before decanting it. The extract was filtered and stored at room temperature in order to be used for further experiments.

2.2. Synthesis of silver nanoparticles

An aqueous solution of silver nitrate was prepared by adding 1 mM of $AgNO_3$ to 50 ml of distilled water at room temperature. The aqueous solution was mixed with 50 ml of leaf extracts at a temperature of 80 °C while stirring magnetically at 1000 rpm for 30 s. The bio-reduced aqueous component was used for the UV–vis spectroscopy characterization.

2.3. UV–vis spectral analysis

The UV–vis analysis was performed by sampling the aqueous component at different time intervals and the absorption maxima was scanned over the 300–800 nm wavelength range on a Perkin-Elmer Lambda 25 spectrometer.

2.4. TEM analysis of silver nanoparticles

Samples for electron microscopy observations were prepared by ultrasonically dissolving the aqueous solution in twice distilled water. A drop of the solution was subsequently deposited onto a lacey C film supported on a Cu grid and allowed to evaporate under ambience conditions. Electron microscopy experiments were carried out in a JEOL 2011 high resolution transmission electron microscope, operating at 200 kV, with a point resolution of 0.23 nm and $C_s = 1.0$ mm. The microscope is also fitted with an Oxford Instruments INCAx-sight liquid nitrogen cooled energy-dispersive X-ray analysis (EDS) detector with an ultrathin window for detailed elemental analysis of the catalysts. Processing of the EDS spectra was accomplished using the INCA Microanalysis Suite software.

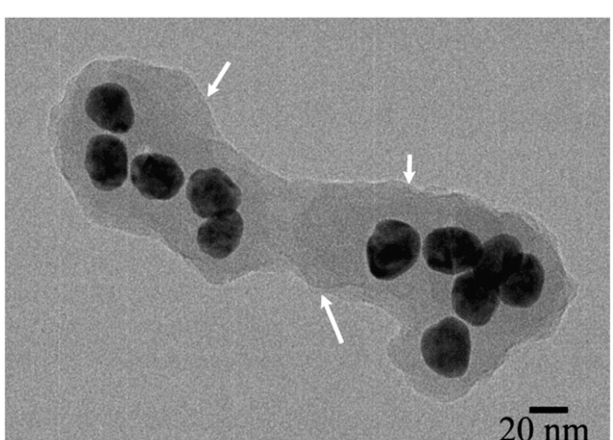

Fig. 2. Typical TEM image of Ag nanoparticles, showing their spherical morphology and agglomeration. The existence of a thin organic layer surrounding the Ag aggregates is depicted with white arrows in the image.

3. Results and discussion

Fig. 1 shows the UV–vis spectra of aqueous component as a function of time variation of leaf broth with 1 mM aqueous $AgNO_3$ solution. Metal nanoparticles have free electrons, which give surface plasmon resonance (SPR) absorption band, due to the combined vibration of electrons of metal nanoparticles in resonance with light wave. The sharp bands of silver colloids were observed at 436 nm. The intensity of absorption band increases with increasing time period of aqueous component and consequent color changes were observed from colorless to reddish yellow. These characteristic color variations is due to the excitation of the of the surface plasmon resonance in the metal nanoparticles.

Transmission Electron Microscopy (TEM) experiments proved the formation of nanocrystalline silver particles, as shown in Fig. 2. The nanoparticles predominately adopt a spherical morphology and are often agglomerated into small aggregates, comprising of 5–6 particles each, as Fig. 2 illustrates. The obtained nanoparticles are quite uniform in size and up to 30 nm. In rare occasions, particles with higher

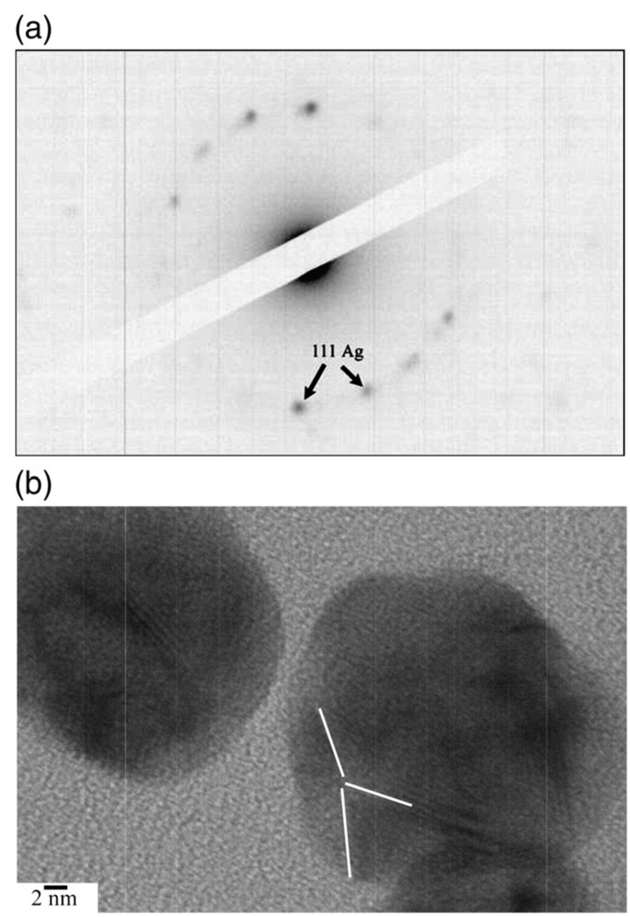

Fig. 3. (a) SAD pattern (invert image) taken from the nanoparticles region. The discrete spots in the ring is characteristic of the single crystalline structure of each individual particle. (b) Higher magnification image of the same area of the Ag particles, illustrating the presence of three-fold twinning in one of them.

sizes were also observed in the sample, but their population was rather low. The TEM images revealed that the small particle aggregates are coated with a thin organic layer, which acts as a capping organic agent. This also may well explain that fact that the nanoparticles showed a very good dispersion inside the bio-reduced aqueous solution, even in the macroscopic scale.

The crystallinity of the Ag nanoparticles was detected by selected area diffraction (SAD) experiments and a typical SAD pattern is depicted at Fig. 3a. The appearance of discrete spots in the ring pattern proved that the majority of the particles are single crystalline materials and they are predominately oriented along their [111] Ag direction, as commonly found for the fcc silver crystal lattice. This was also confirmed by higher magnification TEM images, such as the one showed in Fig. 3b, where the formation of three-fold twinning is demonstrated and further proves the single crystalline nature of the particles. The twin planes are depicted with lines.

Chemical analysis of the produced nanoparticles was accomplished by means of EDS, which confirmed both the existence of Ag and the organic component that covers the Ag aggregates; the latter is implied by the presence of the C, O and Si peaks in the EDS SPECTRA. The EDS analysis also proved that the Ag nanoparticles are in metallic form, with no formation of Ag_2O in them and free from any other impurities.

4. Conclusions

The rapid biological synthesis of silver nanoparticles using leaf broth of Arbutus Unedo provides an environmental friendly, simple and efficient route for synthesis of benign nanoparticles. The size of the silver nanoparticles was between 3 and 20 nm. The bioreduced silver nanoparticles were characterized using UV-V and HRTEM techniques. These reduced silver nanoparticles were surrounded by an organic thin layer. From a technological point of view, these obtained silver nanoparticles have potential applications in the biomedical field and this simple procedure has several advantages such as cost-effectiveness, compatibility for medical and pharmaceutical applications, as well as large scale commercial production.

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