Spectral characterisation of the silver nanoparticles biosynthesised using *Ambrosia maritima* plant

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Silver nanoparticles (AgNPs) were biosynthesised by reducing silver nitrate ($AgNO_3$) using *Ambrosia maritima* aqueous leaves extract. The biosynthesised AgNPs were characterised by transmission electron microscope, Fourier transform infrared spectroscopy and zeta potential analyser. The nanoparticles were generally found to be spherical in shape with average size of 30 nm and were stable at zeta potential of −26.29 mV. The data collected by cyclic voltammetry, ultraviolet–visible (UV–Vis) spectrophotometer and spectrofluorophotometer proved the characteristic electrochemical and optical properties of the biosynthesised AgNPs. The metallic nanoparticles showed an anodic peak at 0.4 mV, a surface plasmon resonance peak at 437 nm and a fluorescence emission peak at the wavelength of 467 nm. In conclusion, AgNPs biosynthesised using *A. maritima* proved to be compatible and feasible to be studied further in *in vitro* and *in vivo* systems. Overall, the biosynthesised AgNPs can be used as a tool applied in a broad range of industrial and medical applications.

1. Introduction: Nanotechnology applications are now widely used and dramatically improve the research in the industrial and medical arenas. The production of nanoparticles becomes indispensable in many situations due to their availability, capability, sustained release and specific targeting [1]. Metal nanoparticles show better accessibility and reliability relative to the large bulk materials. The suitability of the metal nanoparticles was initially evaluated based on the size, distribution, morphology and surface area [2, 3]. Several strategies for synthesis of metal nanoparticles have been tested, often based on chemical methods such as laser ablation, chemical, electrochemical and photochemical reduction [4]. In this regard, the synthesis of metal nanoparticles using biological systems is gathering attention due to the wide range of applications as in biosensors, biolabelling and bioremediation [5, 6]. Bacteria [7, 8], yeast [9], fungi [10–12], algae [13, 14] and plant biomass [15] were exploited as biological candidates in the synthesis of metal nanoparticles.

Plants have played a fundamental role in the field of nanoparticles green synthesis [16]. In the previous studies, *Boerhaavia diffusa* [17], *Plectranthus amboinicus* [4], *Caesalpinia coriaria* [18], *Myrmecodia pendan* [19], *Artocarpus heterophyllus* [20], *Andrographis paniculata* [21], *Phytolacca decandra* [22], *Origanum vulgare* [23] and *Ficus religiosa* [24] represented a more elegant model for the nanoparticles biosynthesis, in particular with silver. The usage of plants over other conventional candidates is preferential as to how simple, fast, cheap, effective and reliable natural medication is [25].

However, to the best of our knowledge, there is no reported investigation that describes the synthesis of silver nanoparticles (AgNPs) by using *Ambrosia maritima* plant. *A. maritima* is an appealing plant for a number of reasons. *A. maritima* (Asteraceae), is widely distributed throughout the Mediterranean region, and well known in Egypt under the name of 'damsissa' [26]. *A. maritime* is an attractive herbaceous plant possessing anti-schistosomiasis, hepatoprotective and molluscicidal properties [27]. In this report, we document the synthesis and spectral characterisation of AgNPs fabricated using *A. maritima* plant leaves extract.

2. Experimental: *A. maritima* leaves were collected and identified by the Egyptian Agricultural Research. Silver nitrate (99.8% pure) was purchased from Cambrian chemicals.

The dried leaves of *A. maritima* were grinded to fine particles using kitchen blender. The aqueous leaves extract was prepared by mixing 2.5 g of the obtained powder with 200 ml of distilled water followed by boiling at 55 °C for 5 min. The extract was filtrated using Whatman filter paper No. 42, kept in the refrigerator at 4 °C and used within a week. About 10 ml of the plant extract was mixed with 150 ml aqueous solution of 0.1 mM silver nitrate and heated for 1 h at 60 °C using a water bath. The solution was centrifuged at 6000 rpm for 40 min.

The morphology and particle size of the AgNPs were characterised by transmission electron microscope (TEM) [JEM-2100 (JEOL), Japan]. The TEM specimen was prepared by diluting a small amount of the AgNPs, before adding it in the ultrasonic apparatus for 20 min. A drop from the aqueous suspension was placed on a copper grid coated with carbon film. The sample was placed in an oven to dry at ambient temperature prior to the spectroscopic examination. An aliquot of AgNPs suspension was subjected to Fourier transform infrared (FT-IR) spectroscopy (IR100/IR 200 spectrometer, USA) measured at wavelength of 4000 to 400 cm^{-1}. Zeta potential analyser (ZetaPALS, Brookhaven) was used to study the stability of the formed AgNPs. The cell was washed by ethanol three times before the analysis. A small aliquot of the purified AgNPs was put on the clear cell then subjected to the apparatus.

Electrochemical measurement was performed using cyclic voltammetry (MF-9002 BASi Epsilon) in a three-electrode setup. The glassy carbon served as the working electrode, a Pt wire as the counter electrode, Ag/AgCl as the reference electrode and pH

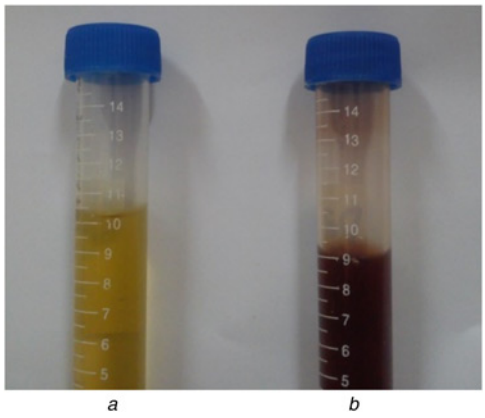

Fig. 1 *Colour comparison between A. maritima plant extract (a) and the biosynthesised AgNPs (b)*

7.4 phosphate buffer solution (PBS) was used as the supporting electrolyte. The cyclic voltammogram was obtained at 100 mV s^{-1} scan rate in the potential range of −1.2 to 1.2 V.

Optical properties were studied using ultraviolet–visible (UV–Vis) spectrophotometer (UV-2450, Shimadzu) and spectrofluorophotometer (RF-5301PC, Shimadzu). The surface plasmon resonance property of the AgNPs suspension was monitored using UV–Vis spectrophotometer. A diluted aliquot of the suspension was taken in quartz cuvette for the analysis at the wavelength of 200–800 nm. The fluorescence emission of the excited electron was determined using spectrofluorophotometer. A small aliquot (0.5 ml) of the AgNPs suspension was diluted 30 times by distilled water before the analysis. The sample was put on quartz cell and subjected to the spectrofluorophotometer for the analysis.

3. Results and discussion: The AgNPs were fabricated by *A. maritima* plant leaves extract. Colour change to brownish (Fig. 1) is regarded as very simple and easy principle to detect the biosynthesis before confirmation by spectroscopic techniques.

Applying TEM technique made it possible to observe the geometry, size and chemical distribution of the biosynthesised AgNPs. The particles size was determined to average volume of 30 nm at 100 nm scale, however a range of 25–50 nm was also common (Fig. 2*a*). The bonding process was reliable and very seldom resulted in incomplete biosynthesis. The particles were taking a pattern of single and polycrystalline diffraction fashion (Fig. 2*b*).

The chemical composition of the nanoparticles suspension was further analysed by FT-IR spectroscopy and the biomolecules bands were seen at 3431, 2937.47, 2864.22 and 1624 cm^{-1} (Fig. 3*a*). The broad band at 3431 cm^{-1} was due to O–H stretching mode and bands at 2937.47 and 2864.22 cm^{-1} are corresponding to C–H group. The observed band at 1624 cm^{-1} is assigned to the stretching vibrations of the C=O bond, while the band at

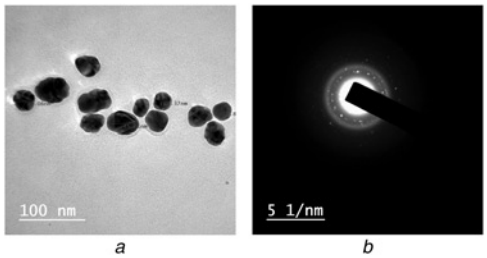

Fig. 2 *TEM images of the biosynthesised AgNPs showing*
a Average size of 30 nm
b Corresponding diffraction pattern

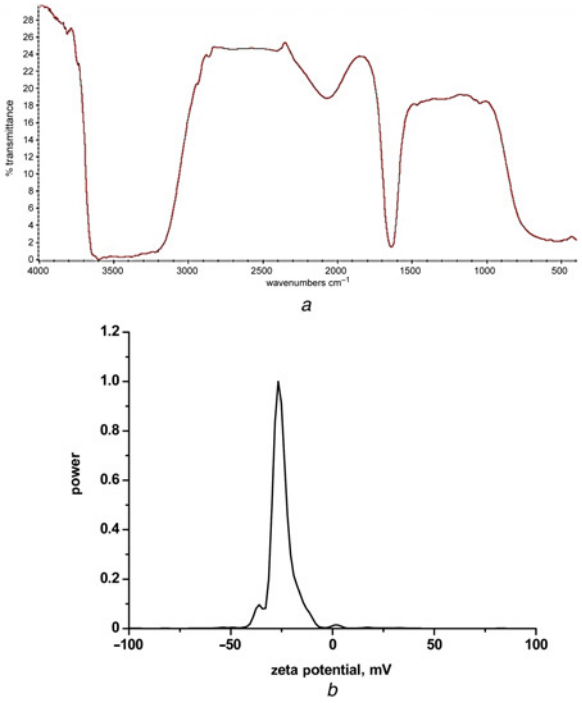

Fig. 3 *Chemical composition of the nanoparticles suspension*
a FT-IR spectrum of the AgNPs suspension showing the peaks of functional groups interacted with AgNPs
b Zeta potential diagram proving the stability of the biosynthesised AgNPs

1047.83 cm^{-1} was attributed to C–O–C stretching mode. Our findings are in agreement with the earlier studies where a specific band at 2073 cm^{-1} was used as indication of the silver atoms reduction [28, 20]. Collectively, these data strongly refer to the involvement of sesquiterpene lactones and flavonoids in the process of nanoparticles synthesis. In addition, the role of the plant biomolecules in the stability of the nanoparticles was studied. The nanoparticles gave a negative zeta potential (−26.29 mV) as shown in Fig. 3*b*. The −25 mV high zeta potential ensured the stabilisation of the metal nanoparticles by making a high-energy barrier [23]. It was also hypothesised that the negatively charged electrostatic repulsive forces possibly maintain the metal nanoparticles [21]. These AgNPs can be used as coating material in many applications. Coating of silica, a filter material used in water treatment, by AgNPs can resist the formation of biofilm in water treatment.

The electrochemical recognition of AgNPs is based on electrode charge transfer when AgNPs strike an electrode as previously described [29]. In our experiments, the biosynthesised AgNPs in PBS suspension of pH 7.4 showed an anodic peak current of

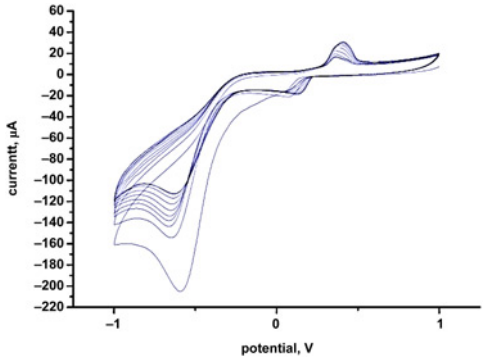

Fig. 4 *Cyclic voltammogram of the biosynthesised AgNPs in the potential range of −1.2 to 1.2 V at 100 mV s^{-1} scan rate*

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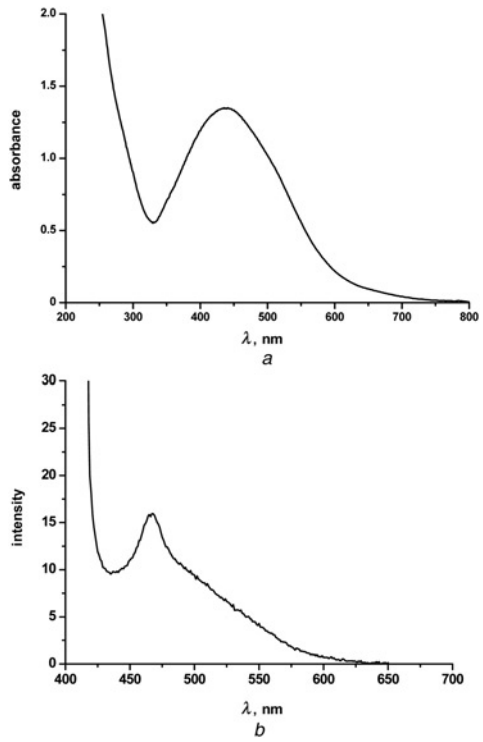

Fig. 5 *Influence of photoexcitation at wavelength of 340 nm from occupied d bands into states above Fermi level*
a UV–Vis absorbance spectrum of the formed AgNPs showing a broad peak at 437 nm
b Fluorescence emission of the biosynthesised AgNPs showing a broad band at 467 nm

30.76 μA at 0.4 mV (Fig. 4). The reduction of the electrogenerated Ag^+ ions displayed electrochemical recognition followed by nucleation of AgNPs at the glassy carbon electrode and the surfaces of AgNPs [30].

The collective oscillation of the silver conductive electrons is often an important criterion for the surface plasmon resonance [31]. AgNPs have better resolution with visible light more than any known organic or inorganic chromophore [32]. It seemed as if the surface plasmon resonance is critically sensitive to the nature, size and shape of the surrounding particles in suspension [17]. As we are interested in knowing the properties of the AgNPs, it was useful to detect the plasmon resonance visible range. As indicated in Fig. 5*a*, the plasmon resonance interacts efficiently forming light with a positive absorption band at 437 nm. The broad band confirms the presence of polydispersed nanoparticles [33]. The fluorescence phenomenon is a three-step process involving photoexcitation of an electron, followed by relaxation of the excited electron, which is accompanied by fluorescence emission [34]. The influence of photoexcitation at wavelength of 340 nm from occupied d bands into states above Fermi level [4] was evaluated and shift of the fluorescence spectrum was observed (Fig. 5*b*). High 467 nm wavelength was associated with low energy release and was accordingly compared with the absorption spectrum shown in Fig 5*a*. The fluorescence shift was related to electron–phonon and hole–phonon scattering process [35, 36]. According to these optical properties, AgNPs can be applicable in optoelectronics as an electrode. This could be embedded in glass or deposited on the top of antireflection layer of the solar cell leading to the reduction of light reflection.

4. Conclusion: We reported the green synthesis and evaluation of AgNPs made by silver nitrate solution and aqueous leaves extract of *A. maritima*. The biosynthesis of AgNPs was detected visually and confirmed by UV–Vis spectroscopy. The geometry and dimensions of the nanoparticles were determined employing TEM. The functional groups involved in the bioreduction of Ag^+ to form Ag (0) nanoparticles and in the capping process were identified by FT-IR spectroscopy. The enhanced surface charge enhanced upon mounting the plant biomolecules onto the nanoparticles was measured using ZetaPALS. The electrochemistry gave a powerful detection signals by the cyclic voltammetry. The surface plasmon resonance and the fluorescence emission peaks were observed by UV–Vis spectrophotometer and spectrofluorophotometer, respectively. The electrochemical and optical properties of AgNPs make them a good candidate for many applications.

5 References

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