

## A green synthesis of nanosilver as a redox electrode for determination of heavy metals

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**Abstract:** Cyclic voltametry, with carbon paste electrodes is a very popular technique in electrochemical studies. Ag nanoparticles was been prepared with *cupressus arizonicx* extract and particle size was reported average 70 nm and carbon powder has been doped with green synthesized Ag nanoparticles. Modified carbon paste electrodes have more responsibility and sensitivity. Standard deviation was reported 0.081 that is valid.

**Keywords:** Cyclic voltammetry, Carbon paste, *Cupressus arizonicx*, Ag nanoparticles.

### Introduction

Plants are a green and echo-friendly source for producing nanoparticles. Use of plants extract as a green reagent and using a carbon paste electrode modified with Ag-nanoparticles in optimized conditions is the aim of this research. Nanoparticles display advantages over macroelectrodes such as enhancement of mass transport, and high effective surface area, when used for electroanalysis. Therefore, much work has been carried out into their formation and characterisation [1]. According to the small size they show unique chemical, physical and electronic properties that are different from the bulk materials. Size, shape, and surface morphology play an important role in nanoparticles properties. Several methods have been used to reduce Ag<sup>+</sup> to Ag nanoparticles [2]. Reduction by sodium citrate and hydrazine are such methods but they use toxic and expensive compounds [3].

The use of various parts of plants and green synthesis in nanoparticles synthesis can be potentially eliminate environmental pollution problems by making the nanoparticles more bio-compatible and non-toxic. Jose-Yacaman and co-workers reported the formation of gold and silver nanoparticles using living plants. Recently silver nanoparticles have been synthesized using various plant products like green tea, natural rubber, starch, etc. plants were occur due to the ketones/aldehydes groups present in the extract which plays an important role in directing the shape evolution in these nanoparticles [4,5]. This paper involves green approach for Ag-nanoparticle synthesis via *cupressus arizonicx* extract. *cupressus arizonicx* were collected from one of the parks in Tehran. Cyclic voltammetry is one of the simple, rapid and powerful methods for characterizing the electrochemical behavior of analytes that can be electrochemically oxidized or reduced. Platinum and glassy carbon electrodes are used in this electrochemical method [6]. A wide variety of nanoparticles have found application in many kinds of analytical Methods. nanoparticles can enhance electron transfer in electrochemical reactions [7]. This study was done by using Ag-nanoparticle s as

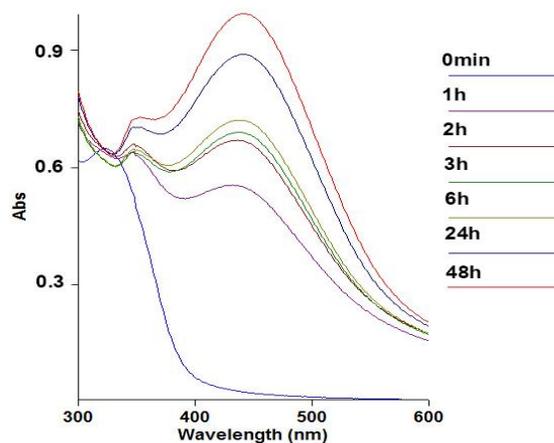
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component of a sensor that detects heavy metal particularly lead (II) ions. When carbon paste electrodes dope with nanoparticles, its efficiency were been evaluated.

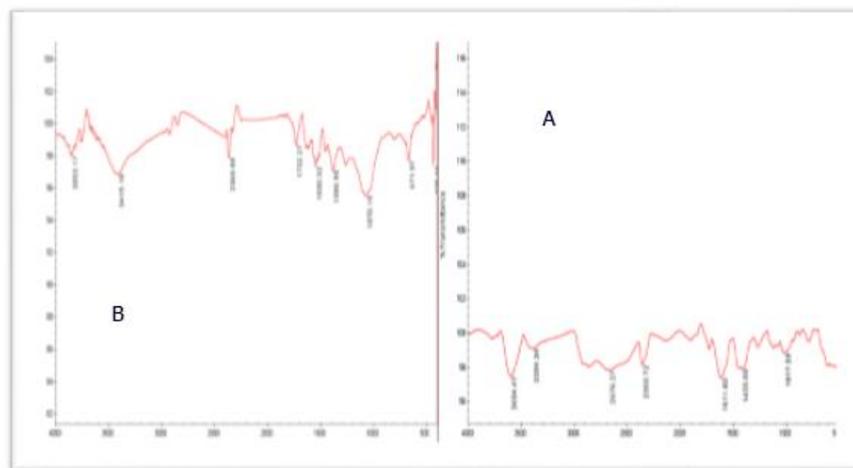
### Results and discussion

Phytochemical reduction of Ag ions using *cupressus arizonicx* extract was established by UV-Vis, XRD, FT-IR and TEM graph. Appearance of yellowish brown color 30 min after adding *cupressus arizonicx* extract to 1mM AgNO<sub>3</sub> solution Related to SPR in the range of 420-450 nm of UV-Vis spectra proved the formation of Ag-NPs [8] (Figure 1).

The 3415.18 cm<sup>-1</sup> strong FT-IR peak of *cupressus arizonicx* aqueous extract deals with phenolic groups and it disappears after phytochemical reduction of Ag<sup>+</sup> ions due to responsibility of hydroxyl groups in reduction of Ag<sup>+</sup> ions (Figure 2).



**Figure 1:** UV-Vis spectra of phytochemical synthesized Ag nanoparticles

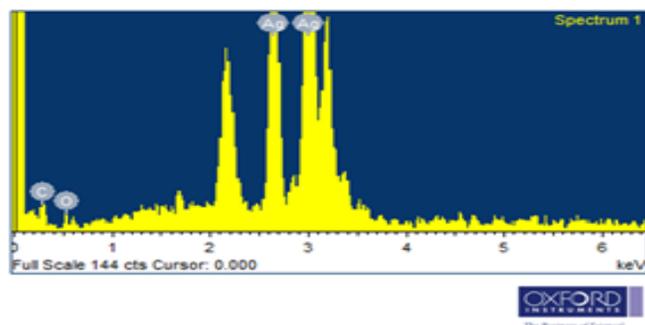


**Figure 2:** IR spectra of plant extract (A) and synthesized Ag nanoparticles

EDX spectra show that 88.15 % of synthesized particles are Ag nanoparticles (Figure 3). XRD spectrum of Ag-NPs shows three intensive peaks at 55°, 46°, 33° and related to (220), (200), (111) HKL values (Figure 4). The Ag-NPs were appeared in a face center cubic (fcc) lattice system. The average size of Ag-NPs was calculated to 70 nm by Debye-Scherrer's equation. The cyclic voltammogram of standard carbon paste and doped carbon paste electrode dipped in lead (II) ions solution is shown in Figure 6 A and B. A sharp peak at -450 to -200 mV indicates the reduction of lead ions. The effect of increasing amount of Ag nanoparticles to carbon powder was analyzed. A maximum current response was obtained for a sensor

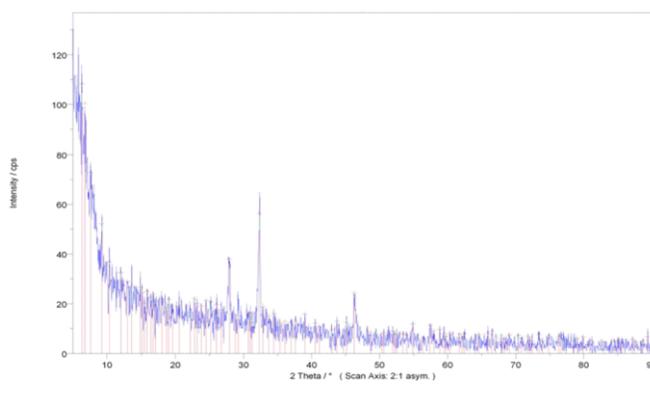
containing 25 % (w/w) Ag-nanoparticles. Carbon is one of the components of electrode and is responsible for its conductivity. Decreasing the amount of the carbon powder will decrease the conductivity of electrode. The optimum pH for the determination of lead using the fabricated sensor is 7. Gardea-Torresday and co-workers achieved the same result in this range of pH. According to them, lead is classed among the metals that are tightly and rapidly bound at pH ≥ 5 and stripped at pH ≤ 2. The voltammogram also showed that at pH higher than 7, the peak current decreases. The decrease in the current response of the electrode at higher pH is due to the formation of the hydroxylic lead complexes. The pH of the supporting electrolyte

showed a significant effect on the electrochemical behavior.

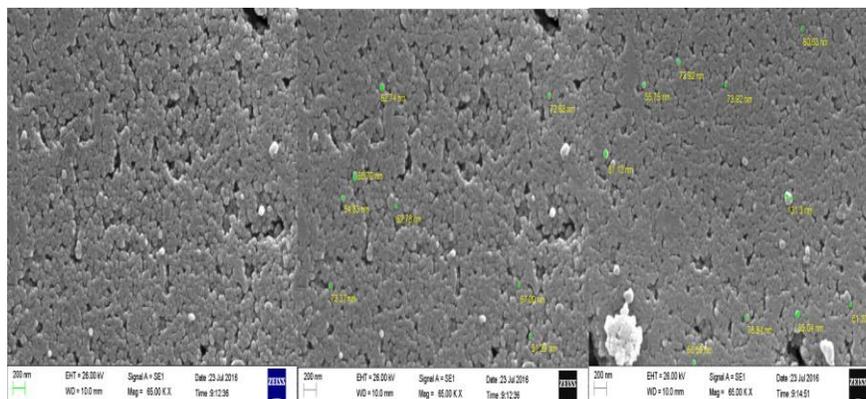


atom	w/w %
C	7.76
O	4.09
Ag	88.15

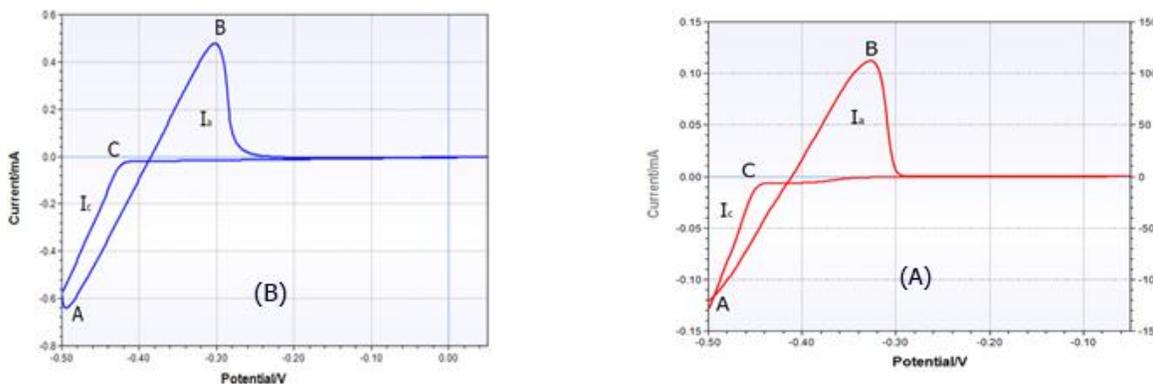
**Figure 3:** EDX spectra of synthesized Ag nanoparticles



**Figure 4:** XRD pattern of synthesized Ag nanoparticles



**Figure 5:** SEM image of obtained Ag nanoparticles



**Figure 6:** Cyclic voltammogram of standard (B) and doped carbon paste (A) electrode, immersed in lead ion solution

As shown in Figure 6 A and B, in doped carbon paste electrode, current density is more than standard electrode and redox reactions are fast. Deposition time is the time required to convert  $Pb^{2+}$  to  $Pb^0$  while imposing a sufficiently negative potential. If a longer time is needed for the reduction, the more cations will be reduced onto the electrode surface. Since more metal cation is reduced onto the surface of the sensor, an enhanced peak current was obtained due to an increased amount of metal cations that were stripped from the electrode surface. When more metal cations were reduced, they would subsequently give an improved peak current.

### Conclusion

As can be seen, in the cyclic voltammetry of  $Pb^{+2}$  solution, one reduction peak (B) is observed and the value of current increased in the modified electrode, which means the presence of Ag nanoparticles enhances the efficiency of the electrochemical reaction on the carbon paste electrode surface. Standard deviation after 5 experiments was reported as 0.081, which is a valid standard deviation.

### Experimental

In this method, 50 g of *cupressus arizonicx* was washed with distilled water and then dried in the air. *cupressus arizonicx* was crushed into small pieces and boiled in 100 ml distilled water (15 min). They were filtered and adjusted to pH 7 by adding 5 ml NaOH. 0.1 M prepared extract was added drop by drop in 100 ml of 10 mM  $AgNO_3$ . The solution was centrifuged at 8000 rpm for 15 min. Nanoparticles were washed with distilled water. Glassy Carbon (GC) substrate was cleaned with distilled water and air dried [9]. Ag-

nanoparticles and mineral oil were mixed with carbon powder to form a paste, then it was packed into the end of a plastic tube (thickness 2 mm) and a copper rod was put up to establish electrical contact. This electrode was used in a three-electrode cell as the working electrode in cyclic voltammetry. A platinum auxiliary electrode and Ag/AgCl reference electrodes were used too [10].

The synthesized electrode was immersed in lead (II) solution. The voltammetric cell contained 0.01 M potassium nitrate solution acting as a supporting electrolyte.

A potential range from -1000 to 1500 mV and a scan rate of 100 mV/s was employed.

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