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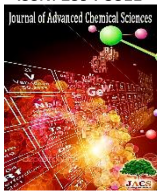

Electrochemical Studies of Biosynthesized Silver Nanoparticles by using *Setaria verticillata* Plant

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ABSTRACT

This study discloses the electrochemical studies, optical property and thermal stability of biosynthesized silver nanoparticles by using *Setaria verticillata* plant extract. The optical property was characterized by X-ray diffraction (XRD) and Thermal gravimetric analysis (TGA). The strong intense peak of XRD indicates the crystallinity of silver nanoparticles. The average size of silver nanoparticles was found to be 24 nm. The decrease in the weight of biosynthesized nanoparticles was due to desorption of biomolecules from silver nanoparticles. The modified GCE reduce the over potential and show well-defined peaks for cyclic voltammetry (CV). The electrochemical result shows that the biosynthesized silver nanoparticles exhibit good electrochemical activity. It can be a route for construction of electrochemical sensors for detection of metal impurities and organic effluents. The modified GCE showed high sensitivity, selectivity and long-term stability.

1. Introduction

Nanoparticles are particles with 1-100 nm in diameter. Nanoparticles play an important role in our day-to-day life. Synthesis of nanoparticles is widely used in many fields such as electronic [1], optic [2], biosensors [3] and drug delivery systems [4]. Nanoparticles have high surface area and chemical reactivity [5]. The properties of nanoparticles can be tuneable by changing size, shape and surface chemistry. Metal nanoparticles are used in medical treatments for cancer, diabetic mellitus and leprosy and tooth ailments [6]. Presently, nanoparticles are coupled with biochemical such as hormones [7], antibodies, proteins and antibiotics for targeted drug delivery systems. The shrinking of nanoparticles depends on the surface energy of reaction mixture. Silver nanoparticles have a high thermal conductivity [8], electrical conductivity [9], optical and catalytic property. The catalytic property of silver nanoparticles degrade effluents. It also converts nitrate and nitrite to nitrogen in chemical fertilizer in controlling environmental pollutants. Silver ions are highly reactive to form a complex with a short lifetime. Metal nanoparticles can be synthesized in many ways like bottom up process and top-down process. Biosynthesis of metal nanoparticles is important today because it is economical, simple and eco-friendly [10].

Weed plants like *Parthenium, Commelina nudiflora, Desmodiumtriflorum* and *Setaria verticillata* are commonly available annual plants around the world. *Setaria verticillata* is considered to be the potential source of useful drugs. It contains phytochemicals such as alkaloids, carbohydrates, saponin, steroid, flavonoids, tannins and phenols [11]. Corrosion studies were carried out by using *setaria verticillata* as a corrosion inhibitor [12]. Phytochemicals act as reducing agents and stabilizing in the reduction of metal nanoparticles. Biosynthesized silver nanoparticles were tested against many cancer cells [13]. Due to the increase in toxic metal contaminants, organic effluents and other heavy metal detection electrochemistry plays an important role in the development of sensors for the detection of contaminants [14]. New electrodes such as silver electrodes, gold electrodes, carbon electrodes, glassy carbon electrodes and other metal electrodes are important in the analysis of harmful organic contaminants. In this study, the optical properties of *Setaria verticillata* mediated biosynthesized silver nanoparticles were characterized by X-ray diffraction (XRD), Thermal Gravimetric Analysis (TGA) and electrochemical studies were focused on Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS).

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2. Experimental Methods

2.1 Synthesis of Setaria verticillata Mediated Silver Nanoparticles [15]

The weed plant *Setaria verticillata* were collected from agricultural lands in Coimbatore, Tamilnadu, India. Analytical grade silver nitrate was purchased from Sigma-Aldrich Chemicals, India. All solutions were prepared by using deionised water. The silver nanoparticles were prepared by mixing 5 mL of *Setaria verticillata* extract with 25 mL of 1 mM aqueous $AgNO_3$ solution under constant stirring. The reaction mixture was stirred at a temperature of 100 °C for 8 hours. The product formed was filtered, dried and stored in a container for further analysis.

2.2 Characterization Studies of Silver Nanoparticles

The synthesized nanoparticles were already characterized by FT-IR spectroscopy, UV-visible spectroscopy, High-Resolution Transmission Electron Microscope (HR-TEM), Selected Area Electron Diffraction (SAED) Scanning Electron Microscope (SEM) and EDAX spectrum [15]. The optical property of biosynthesized silver nanoparticles was identified by X-ray diffraction (XRD) using Shimadzu (PW-6000) X-ray diffractometer, operated at 40 kV and 30 mA. Thermal gravimetric analysis was carried out by using Shimadzu DT-50 thermal analyzer. The crystallite size was calculated by using Debye-Scherer formula

$$D = \frac{K\,\lambda}{\beta\ COS\theta}$$

2.3 Electrochemical Measurements of Silver Nanoparticles

2.3.1 Cyclic Voltammetry

Cyclic voltammetry is used to measure the activity of modified electrodes quantitatively. Several factors are to be considered such as scan rate, the number of scans, upper and lower potential limit. It is an important electrochemical method, where current vs potential curves are recorded at defined applied potential depending upon scan rate. The cyclic voltammetry is carried out at various sweep rates by using Keithley Model 2400 series Source meter and Keithley Model 2182 Nano voltmeter equipment under the nitrogen atmosphere.

2.3.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy is an important tool in electron transfer process. It is also called AC impedance spectroscopy. Impedance spectroscopy is important in distinguishing the dielectric and electrical properties of conducting particles under investigation.

Electrochemical impedance spectroscopy (EIS) measurements are performed with a Potentiostat, Galvanostat and Frequency response analyzer (FRA) under open circuit (not shown) potential in the AC frequency range of 100 kHz to 0.1 Hz with an excitation signal of 10 mV using Solatron Electrochemical Analyzer. The electrochemical cell is performed under a nitrogen atmosphere.

2.3.3 Fabrication of AgNPs Modified GCE Electrode

AgNPs modified GCE electrode is prepared by polishing GCE by using alumina slurry and then sonicated in 1:1 ethanol and water for 2 mins. Then, the GCE surface is dried at room temperature. The biosynthesized silver nanoparticles are dispersed in aqueous solution and sonicated for 1 hour to produce silver nanoparticles suspension. The silver nanoparticles dispersion is coated on GCE by drop casting technique and dried at room temperature. The AgNPs modified GCE electrode is stored under a dry condition at room temperature to carry out further studies. All the experiments are carried out in the nitrogen atmosphere at room temperature.

3. Result and Discussion

3.1 Characterization Studies of Biosynthesized Silver Nanoparticles

XRD analysis was carried out to determine the optical property and crystal structure of biosynthesized silver nanoparticles. Fig. 1 illustrates XRD pattern of biosynthesized silver nanoparticles by using *Setaria verticillata* plant extract. The strong intensity of peaks represents the high crystallinity of silver nanoparticles. The strong peaks observed at 38.65°, 44.42°, 64.66°, 77.25° and 81.83° correspond to hkl planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) respectively. These planes were matched with 2 theta (degree) in the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) plane of silver with face-centered cubic (FCC) crystal structure (JCPDS card no.04-00783) [16]. TGA graph Fig. 2 shows a decrease in the weight of biosynthesized silver nanoparticles which is due to the desorption of biomolecules from silver nanoparticles. A steady weight loss was noticed up to 800 °C and loss of 25% weight from its original weight.

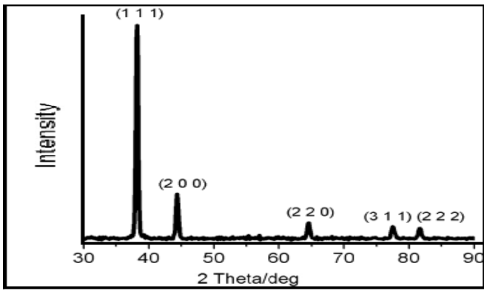

Fig. 1 XRD measurement of biosynthesized silver nanoparticles

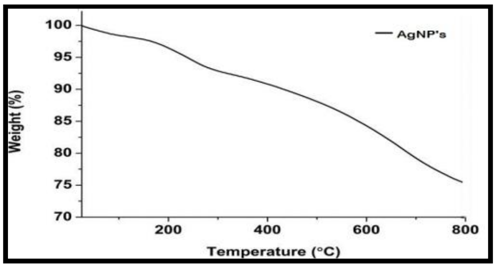

Fig. 2 TGA of biosynthesized silver nanoparticles

3.2 Electrochemical Measurements of Silver Nanoparticles

3.2.1 Cyclic Voltammetry

The cyclic voltammogram demonstrated the electroactivity of the nanoparticles. The biosynthesized silver nanoparticles were characterized for comparison with the GCE electrodes. Fig. 3 shows typical cyclic voltammogram of the biosynthesized silver nanoparticles evaluated in 0.1 molar HCl as well as a bare glassy carbon electrode. The potential scanning from -0.5 to 1.5 V at a scan rate of 100 mV/s. Fig. 3 shows a well-defined redox couple anodic and cathodic peak for the silver nanoparticles. These results prove that the silver nanoparticles show a different redox response compared to the bare GCE. This peak was well defined. Upon increasing the scan rates Fig. 4, the cathodic peak current (I_{pc} 179 μA) increased linearly and cathodic peak potential (E_{pc} 1.24 V) shifted slightly toward the positive side. The corresponding cathodic peak represents the conversion of Ag^+/Ag. The anodic peak current (I_{pa} -159 μA) increase linearly and anodic peak potential (E_{pa} 0.69 V) shifted towards the positive side. The reduction peak shift to more positive potentials indicating electrochemical activity of nanoparticles [17].

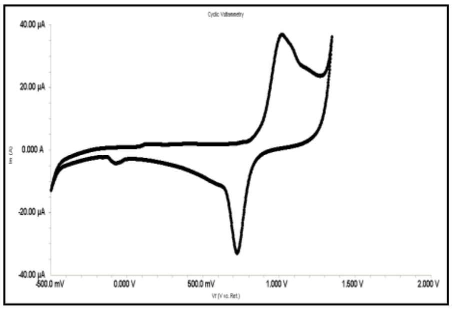

Fig. 3 Cyclic voltammogram of biosynthesized silver nanoparticles in 0.1 molar HCl at a glassy carbon electrode.

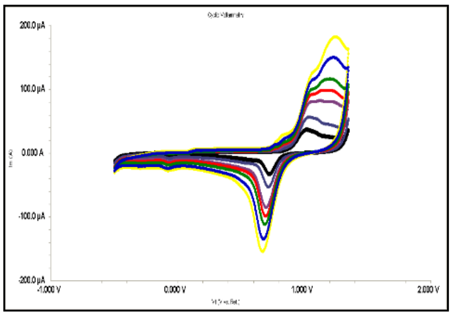

Fig. 4 Cyclic voltammogram of biosynthesized silver nanoparticles in 0.1 molar HCl at a glassy carbon electrode at different scan rates.

3.2.2 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) was carried out to investigate the impedance changes at the electrode surface. The Nyquist plots of modified AgNPs /PCE at different temperatures were shown in Fig. 5. The impedance can be presented as a sum of the real (Z') and imaginary (Z'') components that arises from resistance to capacitance. The shape impedance spectrum and the electron-transfer kinetics can be evaluated. The semicircle parameter corresponds to the electron transfer resistance (R_{et}) and the double layer capacity (C_{dl}) nature of the AgNPs /GCE electrode. The bare GCE exhibits almost a straight line with a very small depressed semicircle representing the characteristics of diffusion limited electron-transfer process on the electrode surface. The biosynthesized modified AgNPs /GCE shows like a depressed semi circle with interfacial resistance due to the electrostatic repulsion by charged surface [18]. This depressed semicircle clearly indicates the lower electron transfer resistance behaviour comparing with the bare GCE [19]. Biosynthesized Ag/GCE electron transfer resistance (R_{et}) has been found as 100 Kohm. The increase in the value of electron transfer resistance (R_{et}) is due to biosynthesized AgNPs /GCE. These results indicate the electrochemical activity of biosynthesized AgNPs /GCE.

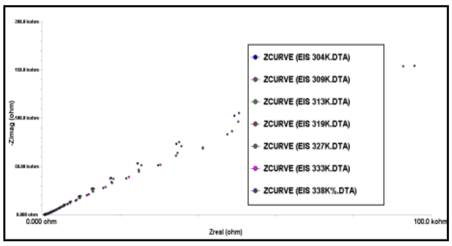

Fig. 5 Nyquist plots for biosynthesized silver nanoparticles at different temperatures

4. Conclusion

The *Setaria verticillata* mediated biosynthesized silver nanoparticles were characterized by XRD and TGA. The optical property of silver nanoparticles was crystalline with a sharp peak. The average size of particle diameter was found to be 24 nm. The decrease in the weight of biosynthesized nanoparticles was due to desorption of biomolecules from silver nanoparticles. The electrochemical characterization of biosynthesized silver nanoparticles by cyclic voltammetry and electrochemical impedance spectroscopy showed good electrochemical activity. Therefore, biosynthesized silver nanoparticles can be used as sensors for nucleophilic and electrophilic species present in the environment. Further investigations may be carried out in this field.

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