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Manufacturing a new electrochemical sensor for the determination of silver ions and its application to X-ray waste

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Abstract: This study includes the determination of ion sliver using a nano electrochemical sensor GE-AgNPs coated on a weir sliver, which was prepared from the reaction of silver nanoparticles AgNPs extracted from tea leaves with drops of sodium hydroxide solution forming a black precipitate from. This precipitate was used to manufacture the selective electrode. This is the first time that this method is applied in the manufacture of selective electrodes without using organic chemical precipitants. The manufactured nanoparticles were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).), and atomic force microscopy (AFM). Also, the properties and specifications of the manufactured nanoelectrod were studied through the optimal conditions, determination of the concentration range, the minimum Nernst response, the minimum electrode sensation, the response time, temperature, the pH range, the calculation of accuracy and compatibility, the calculation of the detection limit, and the response of the electrode to the range of concentrations of (1×10-1-1×109) molar and the correlation coefficient R2 = 0.9993 at a temperature of 30 C˚and the pH range (6-8), the limit of detection (1.0 ×1010)) molar and a response time of (3-10) seconds. The study also included the determination of the selectivity of the manufactured Nano electrode in the presence of a solution of Silver Ions and its successful application on the X-ray Image Waste containing ion sliver.

Keywords: Green Chemistry, Silver Ions, potentiometric, Nano electrode, X-ray Image

1. Introduction

There is a growing need for "green chemistry" methods that involve clean, safe, non-toxic, readily available, and environmentally friendly approaches for synthesizing nanoparticles (1). One of the drawbacks of the physical and chemical methods used in nanoparticle manufacturing is that they are time-consuming, employ hazardous materials and solvents that may be difficult to dispose of, and require substantial energy (2). Consequently, researchers in the field of nanoparticle synthesis and assembly have turned to biological systems for inspiration.

Several single-celled or multicellular organisms are known to produce inorganic materials inside or outside their cells. Currently, biological synthesis of nanoparticles is being explored using plant extracts (1). The significance of nanomaterials primarily arises from their high

surface area-to-volume ratio due to their small size, which increases their surface interactions with other substances (3).

Information has been gathered from various sources by researchers while preparing nanoparticles, where plant extracts act as reducing agents. These plant extracts contain various types of enzymes, vitamins, amino acids, sugars, proteins, polyphenols, and more, which function as reducing agents (4). The reason for choosing plant-mediated biogenic synthesis of silver nanoparticles is that plants contain organic compounds such as flavonoids, amino acids, carboxylic acids, ketones, phenols, and proteins. These substances play a significant role in reducing metal salts and producing nanoparticles using easy, rapid, and environmentally safe methods (5).

Due to the favorable physical and chemical properties of nanocompounds, they are used in the manufacture of sensors (6). Electrochemical sensors are devices that provide information about the composition of a system by chemically coupling a chemically selective layer (recognition element) with an electrochemical transducer. In this way, the chemical energy from the selective reaction between chemical species and the sensor is converted into a useful analytical signal (7). Due to the simplicity of procedures and required equipment, they constitute the largest and oldest group of chemical sensors. They are of great interest today because they can be easily miniaturized and integrated into automated systems without affecting their analytical characteristics (8). Electrochemical sensors operate based on changes in voltage due to chemical reactions (9). (10) This drug was estimated by a sensitive, simple, economical, and cost-effective electrochemical method by preparing a nanoscale electrode from silver nanoparticles easily extracted from tea plant leaves and studying the properties and specifications of this electrode.

I have previously used many chemical and physical methods to manufacture selective electrochemical sensors for the estimation of various ions and drugs in the presence of organic chemical precipitants. These methods are expensive and complicated. Consequently, there is an increasing demand for research into less environmentally harmful, cost-effective methods that require less time and focus on the production of the desired substance. The expanded scientific citation index in the field of nanotechnology has shown remarkable growth during 2020-2021 13-11

Among the easy-to-prepare and environmentally friendly nanoparticle methods is the "Green Synthesis." This method involves using extracts from available plant leaves and roots, with silver prepared using this method demonstrating high efficiency. Researchers have assigned special importance to silver nanoparticles due to their properties such as high thermal and electrical conductivity, chemical stability, high catalytic activity, and antimicrobial activities (12). These particles have proven their effectiveness in the laboratory against cancer cells and possess antifungal activity as well (13) (14).

In this study, a simple green chemistry method was used to prepare silver nanoparticles (AgNPs) from plant extract (tea leaves). These nanoparticles were used for the first time in electrode manufacturing without the use of an organic deposit. An increase in the sensitivity of the manufactured electrode. The analytical study results, concentration determination, electrode response, and establishing the best conditions for obtaining a calibration curve and a linear regression very close to the theoretical Nernst slope were achieved.

2. Materials and Methods

2.1. Instrumentations

The following instruments were used: pH/mV meter (3310 Jenway); silver-silver chloride electrode as working electrode (Jenway); reference calomel electrode (ORION, model 90-01); PVC tubing; Graphite electrode taken from (Battery Mercury Free 777) ; balance (Balance kern ABS 120-4N); magnetic stirrer with hotplate (HPM-10); drying oven (BINDER);. test sieve analysensieb (Hanna Germany)

2.2. Reagents and solutions

$AgNO_3$ powder, Sodium hydroxide (NaOH), dibutyl phetalate (DBP), tetrahydrofuran (THF), polyvinyl chloride (PVC). Acetone, Sulfuric acid , Hydrochloric acid (HCl) , HNO_3

2.2.1. Preparation of Tea Leaf Extract

Weigh 10 grams of tea leaves and place them in a glass beaker. Add 100 ml of deionized water while continuously stirring using a magnetic stirrer. Heat the mixture to boiling at a temperature of 60 degrees Celsius for 30 minutes. Allow it to cool to room temperature. Filter the cooled mixture through a 0.45-micron filter to obtain a clear tea leaf extract and Take 12 ml of the filtered tea leaf extract and gradually add it to 100 ml of 1mM $AgNO_3$ silver nitrate solution under dark conditions and at room temperature.

2.2.2. Sodium Hydroxide Solution 0.1M

To prepare the solution, 0.4 grams of sodium hydroxide were dissolved in a suitable volume of distilled water. The volume was then completed to the mark in a volumetric vial with a capacity of 100 ml.

2.2.3. Preparation of Nanoparticle Precipitate Used in Electrode Manufacturing

The precipitate was prepared by gradually adding the previously prepared silver nanoparticles, with a volume of 100 ml, to 5 ml of a 0.1 M sodium hydroxide solution NaOH while continuously stirring. This resulted in the formation of a black precipitate. Subsequently, it was filtered using a filter paper with a diameter of 0.45 micrometers. After drying the precipitate, it was sieved using a sieve with openings of 300 micrometer.

2.2.4. Manufacturing the Silver Nanoparticle (CG- AgNPs) Electrode

1- Dissolve 0.190 g of PVC in a mixture of 5 ml of acetone with 5 ml of (THF) using an ultrasonic water bath. Add to the mixture 0.1 g of Silver that was prepared in the above paragraph with continuous stirring until complete mixing. To the formed mixture 0.35 ml of plasticizer dibutyl phthalate (DBPH) was added with continuous stirring until homogeneity and thus the membrane solution was ready.

2-The graphite electrode taken from the (Battery Mercury Free 777), which was taken out of the battery, washed, cleaned, and immersed in a sulfuric acid solution for a period of time.

3- Coating stage After preparing the membrane solution in the first stage and preparing the graphite electrodes, the electrode was immersed in the solution mixture for several times until a homogeneous film layer was formed on the surface of the graphite electrode, after which it was left for a sufficient period of time in the laboratory atmosphere for drying.

4- After the electrodes was completely manufactured, it was immersed lead electrode in a solution of silver nitrate at a concentration of 1×10^{-2}M. for a sufficient period of time in order to obtain an exchange of ions. Thus, the electrodes is ready for use in studies and applications, as shown in Figure 1.

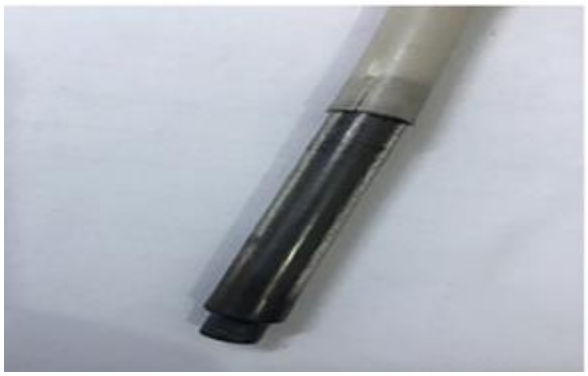

Figure 1: Silver electrochemical sensor

2.3. Characterization of AgNPs

2.3.1. X-ray diffraction (XRD) of silver nanoparticles

it is possible to use plant extracts as reducing and stabilizing agents to obtain pure silver nanoparticles (Ag NPs). This may be due to the chemical compounds present in the plant extracts responsible for the rapid reduction of AgNO3 into Ag NPs in an environmentally friendly one-step process. The crystalline structures of Ag NPs prepared via the polar method using tea leaf extract were confirmed through XRD analysis, as depicted in Figure (2). The results obtained indicate that Ag ions were reduced to Ag NPs by the tea leaf extract. The crystalline dimensions (a = b = c = 9.4 Å) and crystal angles (α = β = γ = 90°) conform to a face-centered cubic (FCC) structure according to JCPDS Card no. 04-0783.

The preference for the (111) direction as the dominant orientation for Ag NPs, followed by (200), (220), (311), and (222), was observed. The enhancement in peak intensity with an increase in pH values indicates an increase in NPs crystallinity. The (111) peak is denser than the other planes, suggesting that (111) is the predominant direction. It is noteworthy that the peaks (Peaks) shifted towards higher 2θ angles with an increase in the silver content, primarily attributed to lattice distortion due to the substitution of silver ions (Ag ions) with ions of smaller ionic radius or due to crystallographic interference.

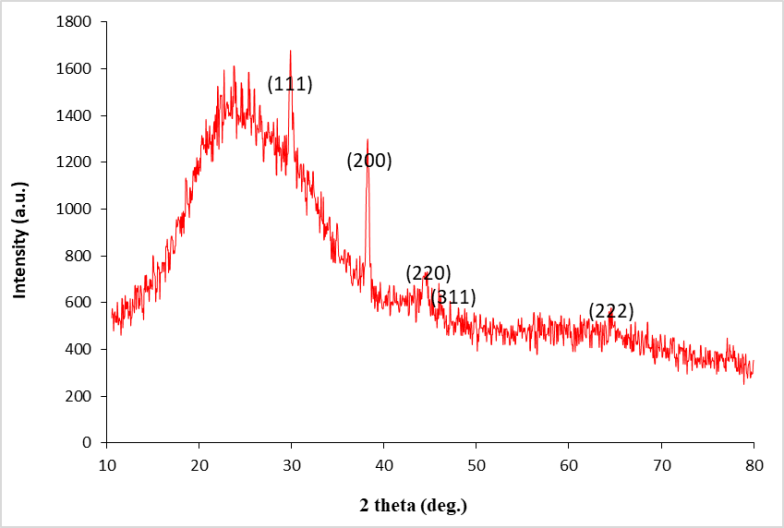

Figure 2: X-ray Diffraction (XRD) Pattern of Silver Nanoparticles.

2.3.2. Transmission Electron Microscopy (TEM) Measurements of Silver Nanoparticles.

From TEM micrographs, it is observed that silver nanoparticles (AgNPs) have a spherical shape, as illustrated in Figure (5-a). This spherical shape provides them with very high efficiency, with only a few aggregations of AgNPs, and their sizes range from 12 to 60 nanometers. They also possess a high surface area, which enhances their sensitivity to polarization, as the high surface area increases the effectiveness at the polarized surface.

Selected Area Electron Diffraction in Figure (5-b) shows that AgNPs are quasi-crystalline, indicating their small size. Furthermore, the precision and clarity of the TEM images align with the results obtained from X-ray diffraction (XRD) in Figure (2).It is worth noting that the use of tea leaf extract in synthesizing silver nanoparticles results in the precise and uniform formation of particles (18).

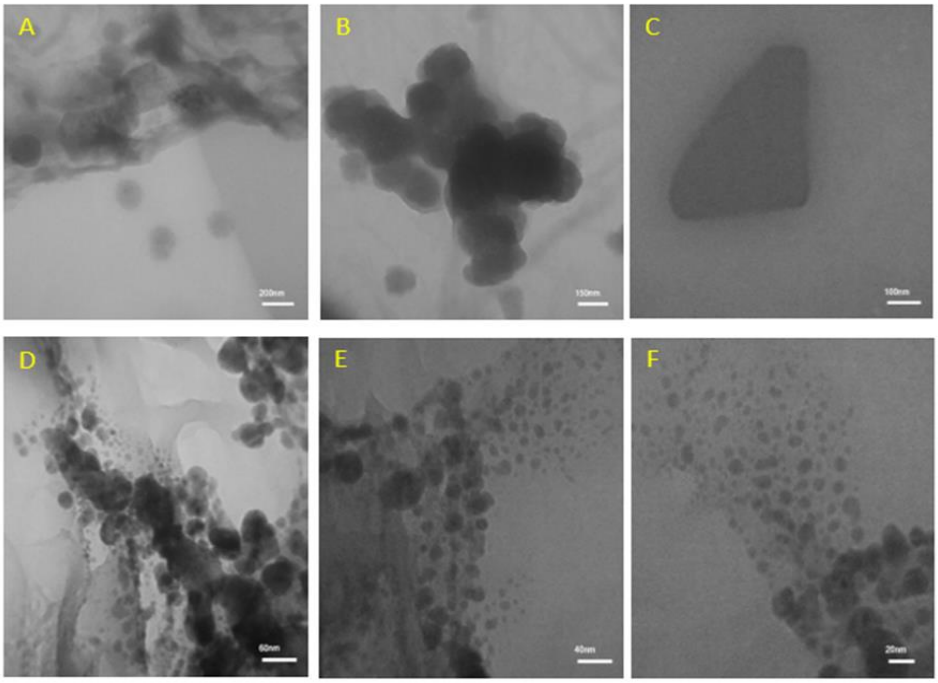

Figure 3: TEM Images of Prepared Silver Nanoparticles (A-F).

2.3.3. Scanning Electron Microscopy (FE-SEM) Measurements of Nanoparticles:

Figures A-F6 illustrate FE-SEM images of silver nanoparticles prepared via the polar method using tea leaf extract, along with a particle distribution diagram across the examined surface area. The FE-SEM images reveal that the particles had spherical or quasi-spherical shapes, with average particle sizes of 11.0 nm, 18.5 nm, and 28.4 nm, respectively.

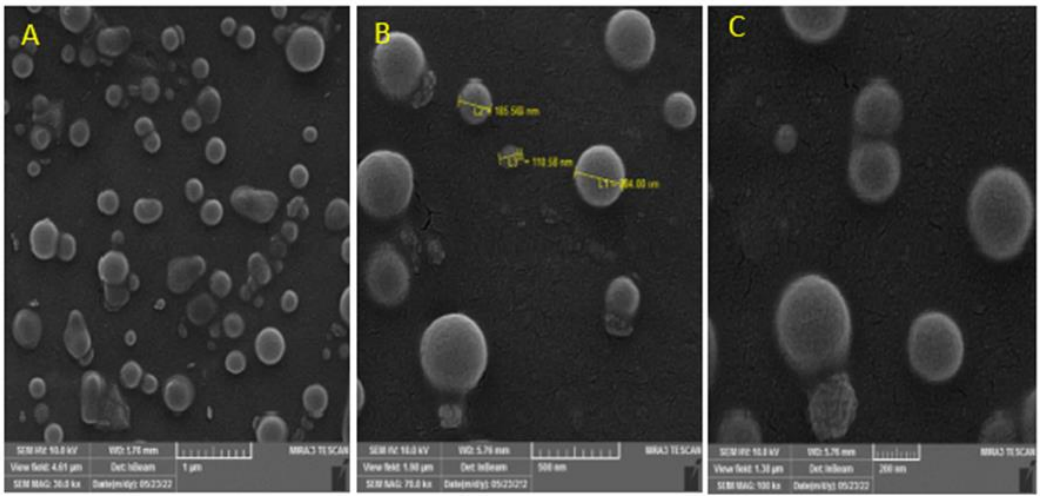

Figure 4: (A, B, C) - Scanning Electron Microscopy of Silver Nanoparticles.

2.3.4. Atomic Force Microscopy (AFM) Measurements of Silver Nanoparticles:

Atomic Force Microscopy (AFM) is a powerful technique for imaging almost any type of surface, including polymers, ceramics, compounds, glass, and biological samples. AFM is used to measure and characterize various forces, including adhesive forces, deformation, and grain size distribution. Figure 5 (A-B) demonstrates two-dimensional and three-dimensional scan operations and profiles extracted from AFM images of AgNPs. From these images, the particle height can be determined. In Figure 6 (A-B), individual and aggregated particles are clearly visible, with an average grain size of 383 nm and a quasi-spherical shape. The particle height, which indicates the average grain size, aligns well with X-ray, TEM, and SEM results (19).

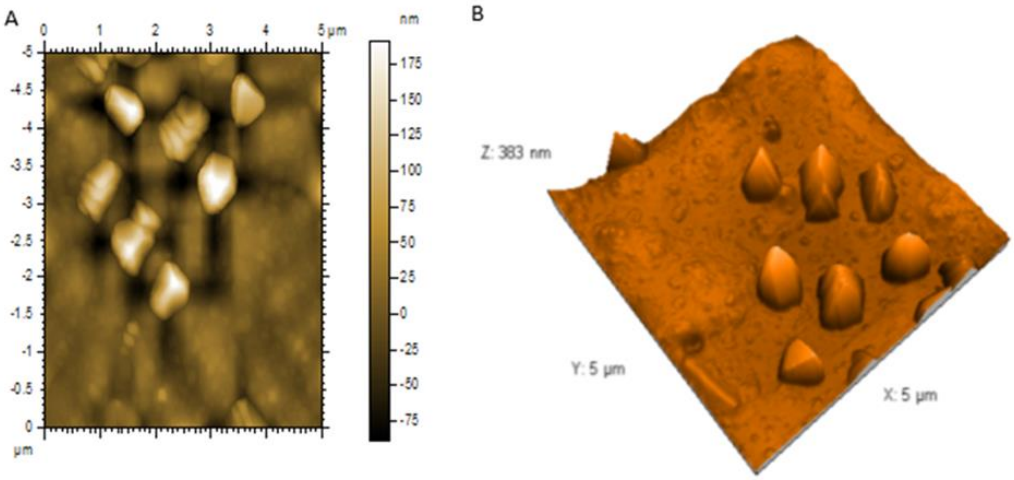

Figure 5: (A-B) - Silver Nanoparticles Atomic Force Microscopy (AFM)

3. Results

This section should provide a concise and precise description of the experimental results, their interpretation, and the experimental conclusions. The section can be divided into the subheadings for presentation clarity.

3.1. Studying the Properties of the Manufactured Nano (CG- AgNPs) Electrode

After selecting the optimal conditions for Nano sensor fabrication, the minimum polarization sensitivity and the minimum non-Nernstian response were calculated using the stress method. This was achieved by measuring the voltage rate for each concentration three times compared to the reference electrode at pH 6 and a temperature of 30 degrees Celsius. Additionally, the response time of the manufactured Nano sensor was studied for the samples.

3.2. Effect of pH

The pH effect of the test solutions on the potential response of the proposed electrode was investigated over the pH range (6-10) for $1x10^{-2}$, $1\times 10^{-4}$and $1x10^{-6}$ M of Ag^{+} ion solutions. The data obtained show that, the electrodes gave pH, (6-8). As shown in figure (6), at a pH value higher.

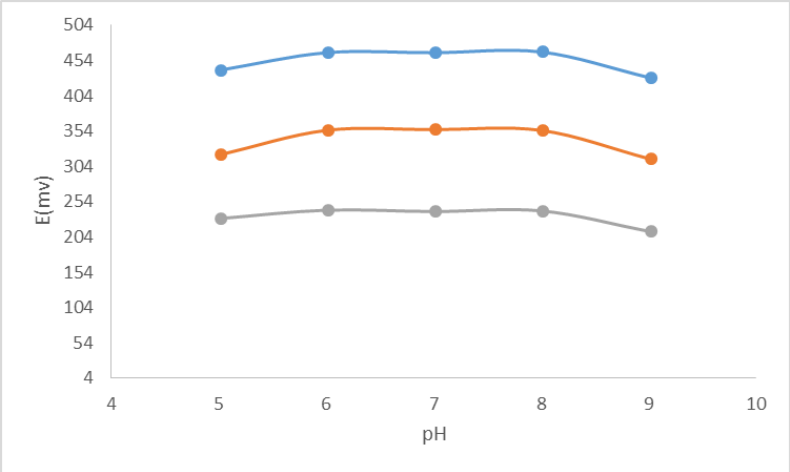

Figure 6: Effect of temperature the response.

3.3. Effect of Temperature

We studied the effect of changing the temperature from 15 to 55°C on the voltage of the electrode that was synthesized for two different concentrations $1x10^{-2}$, 1×10^{-4} and $1x10^{-6}$ M of the standard solution of Ag^{+} ion. We studied each concentration separately and the results are shown in Figure 7.

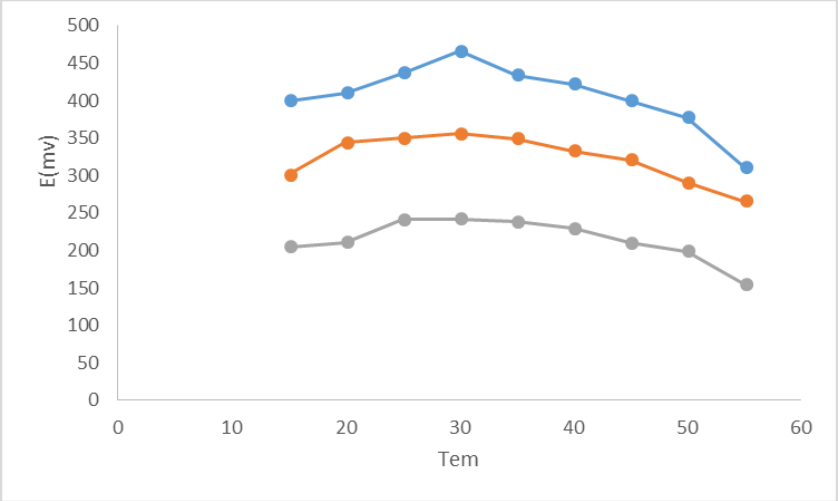

Figure 7: Effect of temperature the response.

3.4. Response Time

Figure (8) shows the response time of the two electrodes, as it is noted that the response time for the electrode Ag+ within the range of concentrations between 10^{-1}- 10^{-9}M ranged between (3-27) seconds, and it is noted that the response time of the electrode is inversely proportional to the concentration of ions in the external solution.

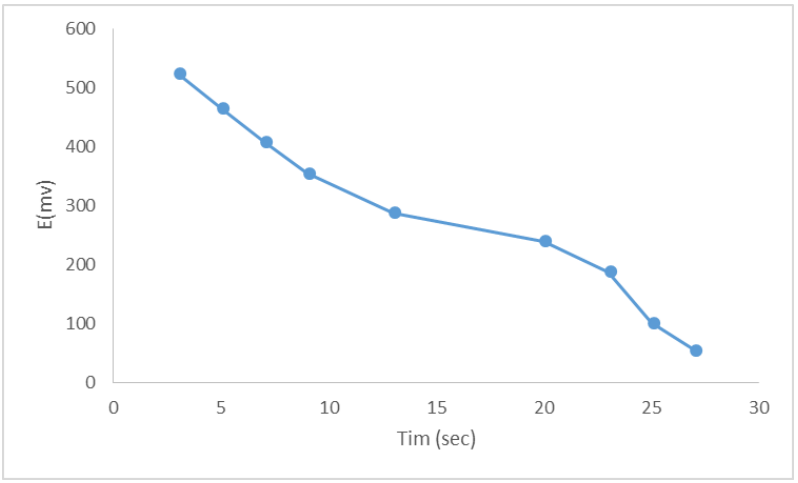

Figure 8: Response time the electrode.

3.5. Calibration Curve

After testing the manufactured Nano electrode, a series of different concentrations of silver ion solution was prepared and measured under the selected optimal conditions. A calibration curve was plotted, representing the relationship between voltage change (mv) and concentration change (expressed –log [ion]), as shown in Figure 11 and Table 1. Through statistical data processing and the use of relevant equations, correlation coefficient, linear percentage, slope, and relative standard deviation RSD % were calculated, as indicated in Table 3. The results in Table 3 demonstrate that the manufactured coated Nano electrode exhibits high selectivity and sensitivity.

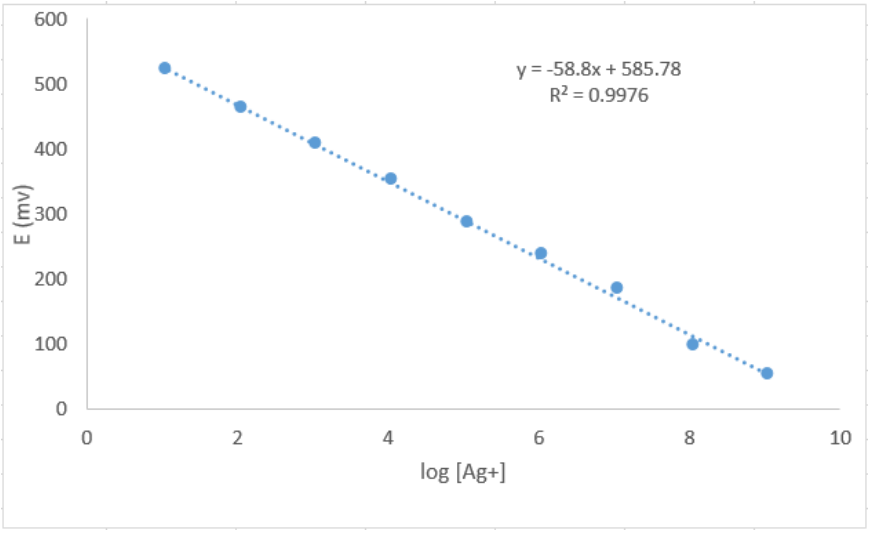

Figure 9: electrode Calibration Curve.

Table 1: Statistical Values for the Calibration Curve of the Nanoelectrode.

The Manufactured Electrode	Conc. of Ag^{+1} (M)	Conc. found (M)	RSD%	Rec%
CG-Ag NPs	1×10^{-1}	1.015×10^{-1}	0.0087	101.5
	1×10^{-2}	1.010×10-2	0.0091	101.02
	1×10^{-3}	0.9905×10^{-3}	0.2533	99.05
	1×10^{-4}	0.9879×10^{-4}	0.013	98.79
	1×10^{-5}	0.9955×10^{-5}	0.054	99.55
	1×10^{-6}	1.0020×10^{-6}	0.011	100.2
	1×10^{-7}	0.9920×10^{-7}	0.0320	99.20
	1×10^{-8}	1.0100×10^{-8}	0.0124	101.0
	1×10^{-9}	0.9964×10^{-9}	0.0416	99.64

Table 2: Conclusions of the Study on the Nature of the Manufactured Nanoelectrode.

The Manufactured Electrode	Response Time(sec)	Detection Limit of the Electrode(M)	The Minimum Nernst Response Limit (M)
CG- AgNPs	5-20	1×10^{-10}	1×10^{-9}

Table 3: Summary of Values for Slope (a), Intercept (b), and Correlation Coefficient (r).

Correlation Coefficient (r)	Linear Range of Concentrations	Measured Concentrations	Intercept b	Slope a	The Manufactured Electrode
0.9988	10^{-1}-10^{-9}	9	585.78	-58.8	CG- AgNPs

3.6. Accuracy and Precision

Following the calibration curve construction for the manufactured electrode, accuracy and precision were assessed by measuring voltage values for a number of concentrations falling within the linear range of the calibration curve. This was done with an average of six readings per concentration, under the selected optimal conditions. The results are presented in Table 4.

Table 4 demonstrates that the recovery percentage does not exceed 103%, and the highest value for the relative standard deviation for the electrode under study is 0.123%. These results indicate that the manufactured Nano electrode exhibits high accuracy and precision.

Table 4: Values Accuracy and Precision .

The Manufactured Electrode	Conc. of Ag^{+1} (M)	Conc. found (M)	Rec%	RSD%
CG- AgNPs	1×10^{-2}	1.008×10^{-2}	100.8	0.099
	1×10^{-4}	0.99×10^{-4}	99.0	0.106
	1×10^{-8}	1.03×10^{-8}	103.0	0.120

3.7. Selectivity of CG-Ag NPs electrode

Table (3) shows the values of selectivity coefficient. The selectivity coefficient ($K^{A,B}$ pot) of CG-Ag NPs electrode for determination Ag^{1+} ions towards different cations and anions were determined by mixed solution method. The concentration of Ag $^{1+}$ ions were (1×10^{-2}, 1×10^{-4}) M and the concentration of interfering ions were 10^{-2} M. The calculation formula of and interfering ion are equal.

Table 3: Values of selectivity coefficient.

Interfering ion of 1×10^{-2} M	CG-Ag NPs electrode	
	Conc. of Ag^{+1}(M)	
	1×10^{-4} M	1×10^{-2}M
K^{+1}	0.0003	0.0007
Br^{-1}	0.0047	0.0023
Cu^{+2}	0.0055	0.0043
Cr^{+3}	0.00061	0.0091
SO_4^{-2}	0.00053	0.0027
Zn^{+2}	0.0019	0.0067

3.8. Lifetime of CG-Ag NPs electrode

Figure 10 Show lifetime of CG-Ag NPs electrode. The lifetime for each of electrode (90) days Straight. After that, CG-Ag NPs electrode appeared a negative shift, may be attributed to leakage the membrane constants of the polymeric based.

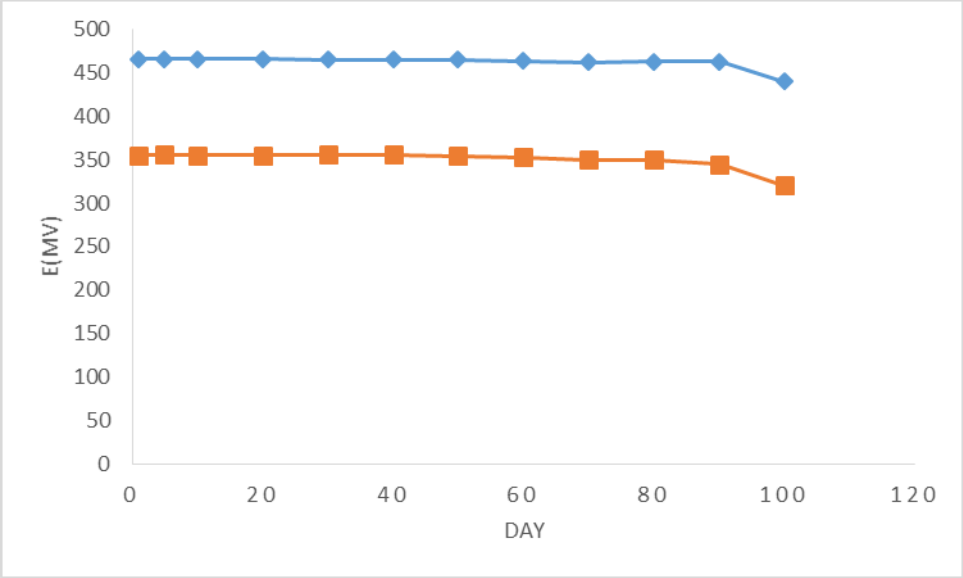

Figure 10: Time life of the electrode**.**

3.9. Applications

The X-ray photographic films were collected in nine pieces (dimensions 25 cm × 30 cm) They were washed with distilled water, then cut into smaller pieces, with a total weight of 171 grams. Subsequently, they were treated with a solution consisting of 250 ml distilled water and 500 ml nitric acid for 3 hours to form a silver nitrate solution. The solution was separated, filtered to remove impurities, and washed with water several times. Afterward, 150 ml of hydrochloric acid with a concentration of 12.04 M was added, resulting in the formation of a white precipitate. The precipitate was washed with hot water several times. Following this, a solution of 1 M sodium hydroxide was added, filtered, and dried on a hot plate for a specific duration.

Table 6: Application of Manufactured Nano silver (AgNPs) on X-ray Waste.

The Manufactured Electrode	Concentration of the unknown silver	Theoretical silver concentration	Rec%
CG- AgNPs	0.98×10^{-3}	1.00×10^{-3}	0.98

4. Conclusions

The following conclusions were drawn from the obtained results:

1. Preparation of silver Nano dots via a straightforward green method using tea leaf extract and their utilization as a sensor for silver ions.
2. The manufactured electrode exhibits remarkably high sensitivity, capable of detecting concentrations as low as (1×10^{-10}) molar, higher sensitivity.
3. Rapid response time, coupled with outstanding selectivity and high sensitivity.
4. Ease of measurement without contamination from environmental factors and immunity to external conditions.
5. Successful application of the manufactured electrode to X-ray waste materials

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