

Polyol synthesis of Ag Nanowires as an electrochemical sensor for the quantification of Carcinogenic Hydrazine

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In this work, we have developed Silver nanowires constructed by the sustainable polyol method. The as-synthesized nanowires are isolated and characterized with various spectroscopic methods like UV-Visible spectrophotometer, X-ray diffraction, and surface morphology analysis through Scanning Electron Microscopy (SEM). The entire analysis has well explained the formation of nanowires proceeded to be an electrocatalytic sensor. To investigate the electrocatalytic activity of as-synthesized silver nanowires, cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) systems were utilized. The silver nanowire fabricated over GCE and applied as an electrocatalyst sensor towards the determination of carcinogenic Hydrazine. To investigate the lower concentration ranges and detection limit differential pulse voltammetry method were used. The fabricated sensor gives a very good linear range and the limit of detection for determination of hydrazine was attained to be 0.01 - 260 μM and 0.06 μM correspondingly. The as-prepared AgNWs/GCE exposed superior selectivity, storage stability, and reproducibility for the determination of Hz. On affording the above-stated conclusions, we expectantly tested our proposed sensor for real-time monitoring.

Keywords: silver nanowires, polyol method, Carcinogen, Hydrazine, Differential Pulse Voltammetry.

1. INTRODUCTION

Metal nanowires have been widely investigated in terms of optical properties and applied as conductive fillers to improve adhesive behaviors [1,2]. They are one-dimensional (1D) nanostructures. Later, Silver has superior physicochemical properties than other nanostructured metals. Among various

metal nanowires, Silver nanowires (AgNWs) has fascinating abundantly more courtesy owing to their extraordinary optical, electrical, thermal and mechanical properties. The AgNWs are scrutinized as the most auspicious material in flexible electronics owing to their mechanical properties. Hence the bulk manufacture of AgNWs remains essential and of prodigious importance. Metal nanowires can be manufactured by predictable chemical and physical methods [3-5]. However, the extensively detained of the existing chemical synthetic progressions are stared as consuming a moderately high scale. There is cumulative much concern by the researchers to enhance hygienic, and harmless synthetic procedures. A moderate material presenting advantages than TCE is meta nanowire like (Silver nanowire; AgNWs) engages which are formerly made-up with highly transparent in nature [6]. AgNWs engages similarly consume the qualities like existing flexible through numerous twisting sequences besides can be generated and dropped at lesser temperatures than TCOs [5]. AgNWs were synthesized by the simple polyol technique. In this method, the nanowires ingenious yield a very large amount by reducing AgCl into AgNWs with the help of Ethylene Glycol, and polyvinyl pyrrolidone (PVP) surfactant and the overall progress implemented by copper chloride solution [3]. Moreover, the polyol process also harvests noteworthy quantities of nanospheres, nanoplates and nano bars. The amount of these materials are precise by thermodynamic and kinetic aspects throughout the preparation with a maximum ~70% nanowires consuming attained [7]. The elasticity of silver nanowires greatly might be modified to discover numerous applications in various field of nanomaterials and electronics [8-10].

The electrochemical determination of Hydrazine (Hz) is very much significant to human life and the aquatic environment. It was a direct methyl derivative, neurotoxic, carcinogenic and mutagenic effects and caused serious hazards to public health and the environment. It had been used in the propellants in rockets, aerospace industries, fuel cells, agriculture, catalytic applications, pharmaceutical industry and reducing agents, it has been described that Hz has been implicated in the terrorist incidents [14-19]. The accidental release may cause series of ill effects. Exposure to hydrazine could affect the central nervous system (CNS), liver, kidney and also demonstrated as a feasible human carcinogen by the Environmental Protection Agency (EPA) [20]. Consequently, efforts have been made to grow electrochemical sensitive methods for the determination of Hz. The development of various methods like potentiometry, chromatography, amperometry, voltammetry for the quantification of Hz is important due to its essential in industry and it is poisonous [21]. Formerly, electrocatalytic techniques are more predominant, since they were easy handled and exposed superior sensitivity, selectivity, time-consuming, and highly reproducible. [22-27]

The rapid detection of very lower concentrations of analytes and biological drug molecules by reasonable procedures is of prodigious attention in investigative chemistry. The development of preferred sensor and its usage could be fascinating properties like ease of access, fairly quick response, economical consumption, simple synthesis method and wide linear range.[28]. AgNWs are predominantly exciting to construct and investigate owing to bulk silver shows large electrical and thermal conductivities [29-31]. Herein, we reported that when Ag nanowire was to be prepared through polyol method for the electrochemical quantification of Hz. The AgNWs modified electrode displayed the superior response constancy and excellent electrocatalytic activity towards the electrochemical detection of Hz without any chemical changes on the surface, which can be proficiently used for the valuation of Hz.

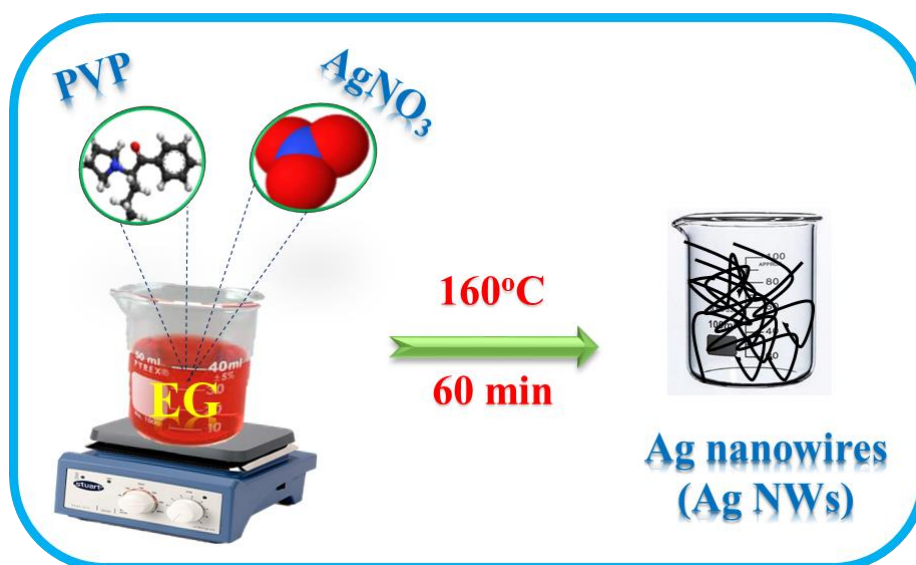
2. EXPERIMENTAL SECTION

2.1. Chemicals and reagents

Silver Nitrate (AgNO_3), Copper Chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), Ethylene Glycol (EG), Polyvinyl Pyrrolidone (PVP) and all the other chemicals and reagents were bought from Sigma-Aldrich chemical company (USA). The monosodium phosphate (NaH_2PO_4) and disodium phosphate (Na_2HPO_4) were used for the preparation of electrolyte solution. NaOH and HCl are used to attain the various pH of the supporting electrolyte. Doubly distilled water (DD water) was used throughout the experiment for the preparation of reagents and compounds.

2.2. Instrumental Methods

The optical properties of the as-synthesized Silver nanowires were evaluated using a UV-Visible/NIR spectrophotometer (JASCO V-770), The crystalline nature of the nanowire was characterized with help of XRD XPERT-3 analyzer with $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$). The morphological examinations of synthesized Ag Nanowires were scrutinized using Scanning electron microscopy (JEOL-JSM-6360 instrument, USA). The CV investigations were evaluated with help of a CHI 660A electrochemical instrument from the United States and a Gamry model 330 from the United States. The Platinum wire used as counter and glassy carbon (GCE) electrode (3 mm dia) as a working electrode, Ag/AgCl (satd. KCl) as reference electrode respectively. The alumina polished GCE were precleaned with water and 5 mg/mL silver nanowire was sonicated for 20 minutes to attain homogeneous suspension. Latterly 8 μL of the suspension drop cast over the GCE surface and used for all the electrochemical experiments.



Scheme 1. Schematic representation for the synthesis of Silver Nanowires (AgNWs)

2.3. Synthesis of AgNWs by polyol method

The polyol method entails reducing a salt of metal precursor with a polyol, which is a chemical compound of multiple hydroxyl (-OH) groups. Polyol and Ethylene glycol used in this preparation, assisted as both a dropping agent and a solvent. 5 mL of EG was heated for one hour at 160°C with stirring at 260 rpm. Then, it has been immersed in an oil bath with glass vials. Furthermore, adding a 40 ml of 4 mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ethylene glycol solution were heated for 15 min. Each vial was filled with 1.5 mL of 94 mM AgNO_3 and ethylene glycol, consequently 1.5 mL of 114 mM PVP and ethylene glycol were added. Pipettes were used to deliver all reagents. After about an hour, the reaction was halted when the solution turns in to gray and wispy. Submerging the vials in cold water halted the reaction. The final product was washed three times with deionized water and once with acetone [32].

3. RESULTS AND DISCUSSION

3.1 Characterizations of AgNWs

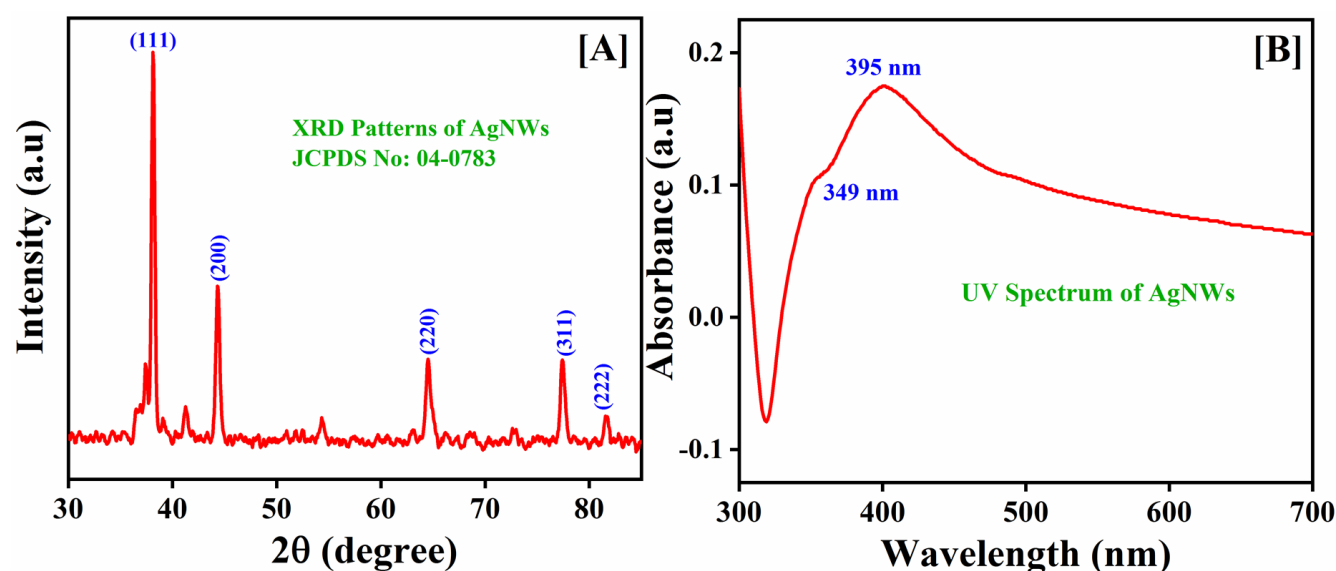


Figure 1. [A] X-ray diffraction patterns and UV-Vis absorbance of AgNWs.

The crystalline nature of the AgNWs were investigated by XRD techniques. Fig. 1. [A] displays the X-ray diffraction peaks obtained at 2 theta angles 38.3°, 44.4°, 64.4°, 77.4° and 81.6° which are in good relationship with lattice planes (111), (200), (220), (311) and (222) and were well matched with the previous work and the JCPD number of 04-0783 correspondingly [31]. The large diffraction peaks at lattice planes (111) and (200) reveals successful formation of AgNWs. Fig.1 [B] denoted as the UV-Visible absorbance of AgNWs shows two distinctive peaks obtained at 349 and 395 nm. These two specified peaks were correlated the transverse resonance mode with its one dimensional cross-sectional view of silver nanowires. The absorbance falls at the wavelength 349 nm were said to be attributed to the out-of plane quadrupole resonance, whereas the broad peak falls at the wavelength 395 nm were

seems to be ascribed, vice-versa. Moreover, the longitudinal mode of the as-synthesized Ag NWs extinct perhaps owing to the moderately large aspect ratio [33]. The morphological analysis of the synthesized AgNWs characterized by SEM and observed results are displayed in Fig. 2 [A-D]. It can be seen that the 1D AgNWs reveal smooth wires without any agglomeration and confirms the formation of silver nanowires.

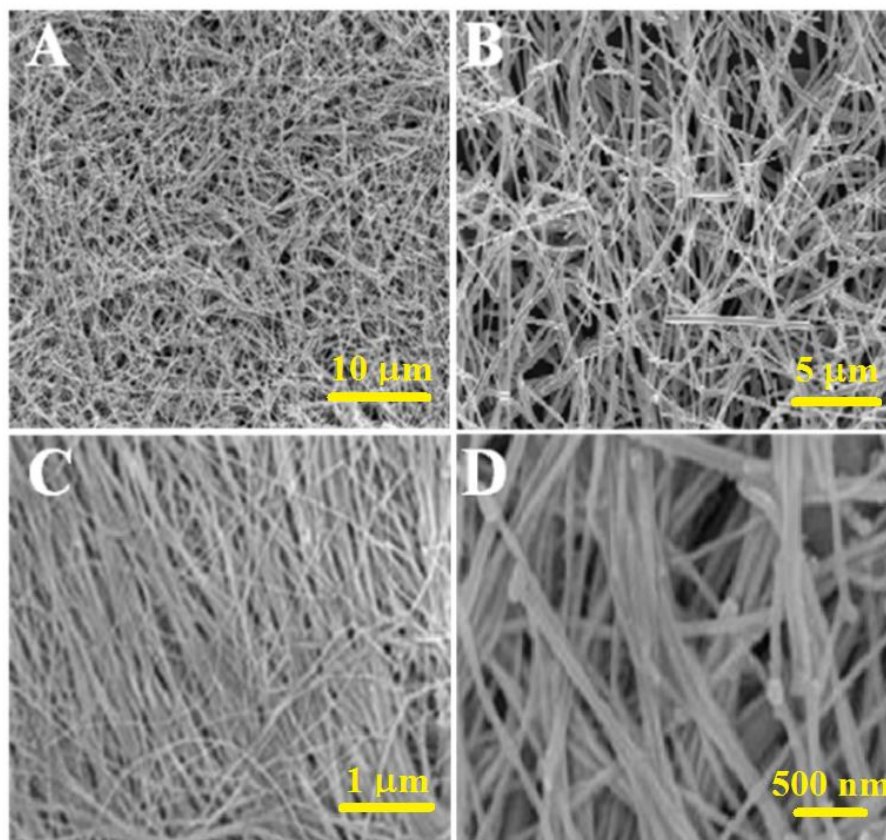


Figure 2. [A-D] SEM images of AgNWs with different magnifications.

3.2. Electrochemical oxidation of Hydrazine at AgNWs/GCE.

The electrocatalytic oxidation of Hz with AgNWs modified and unmodified GCE in presence of 0.05M PBS (pH 7.0) at 50 mV/s scan rate was analyzed using cyclic voltammetry and the observed CV signals displayed in Fig. 3A. From Fig. 3A the unmodified GCE exhibits small CV signal in presence of 250 μ M Hz owing to the weak electron transfer and poor active surface area of the unmodified GCE. Alternatively, the AgNWs modified GCE shows superior oxidation peak current at (V) peak potential in presence of the same amount of Hz. It should be noted that the AgNWs modified GCE provides a higher anodic response owing to the physicochemical properties such as good electrical conductivity, larger surface area, and a greater number of active sites of the AgNWs. Through the CV experiment, there is no anodic oxidation response obtained without the presence of Hz. Additionally, the bar chart for the electro-oxidation of AgNWs/GCE and bare GCE displayed in Fig.3B.

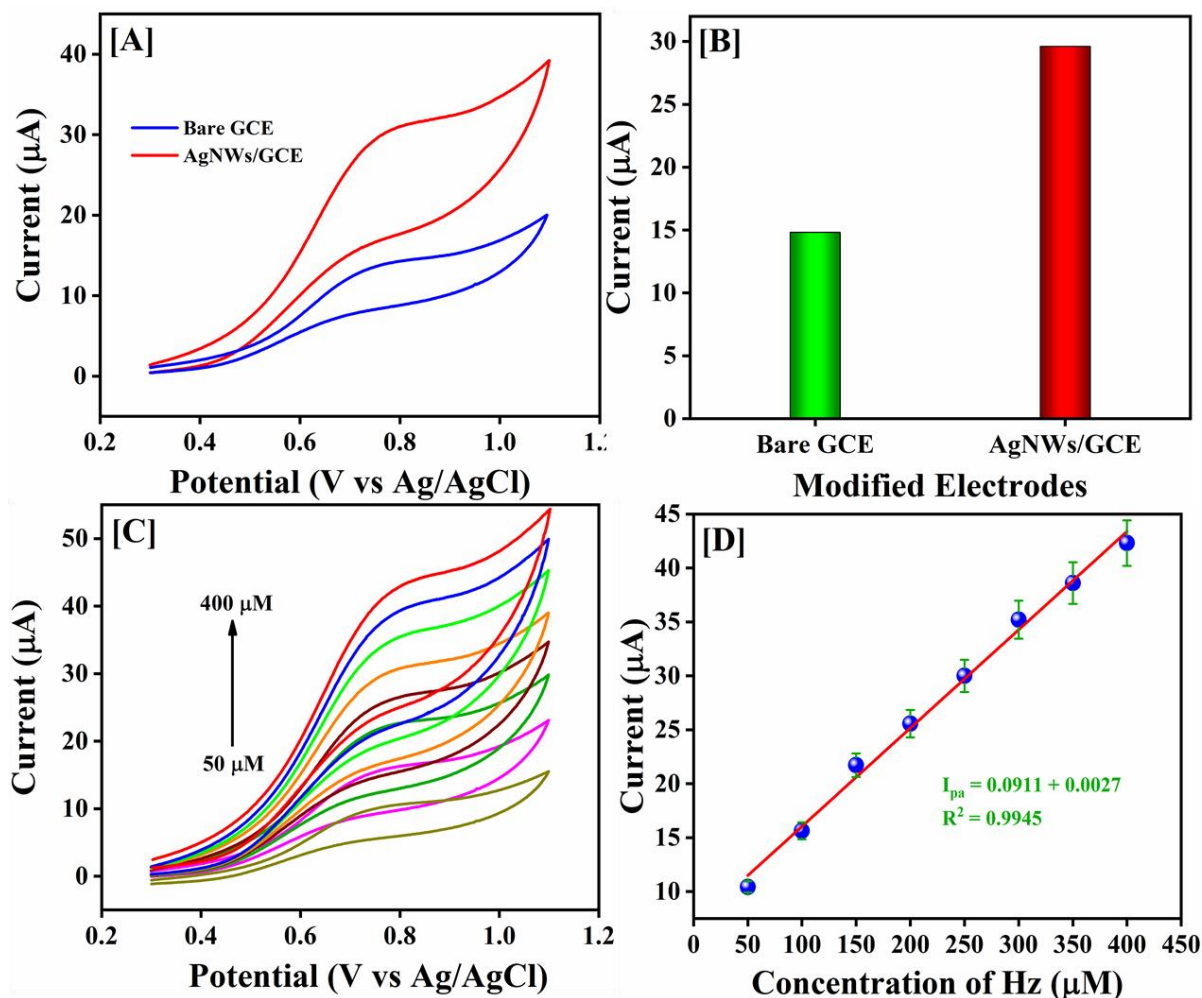


Figure 3. [A] CV signals of AgNWs modified GCE and Bare GCE, [B] Corresponding bar diagram for different modified electrodes against CV current, [C] CV signals for Hz oxidation on AgNWs/GCE at various concentrations, [D] linear plot between the quantity of Hz and anodic oxidation current. AgNWs/GCE at various concentrations, [D] linear plot between the quantity of Hz and anodic oxidation current.

The electrocatalytic activity of the AgNWs/GCE was scrutinized using different quantities of Hz in 0.05M PBS (pH=7.0) at 50 mV/s sweep rate by CV and obtained signals shown in Fig.3C. The anodic oxidation response increases with increasing the quantity of Hz from 50 to 400 μM . The oxidation peak grows steadily with increasing quantity of Hz and anodic peak response linear plotted against the quantity of Hz displayed in Fig. 3D. The linear fitting equation and correlation coefficient wrote as $I_{pa} = 0.0911 + 0.0027$ and $R^2 = 0.9945$. These results proposed that the AgNWs/GCE shows excellent electrocatalytic activity towards Hz sensor. In addition, the charge transfer performance of AgNWs/GCE was inspected on differentiating scan rate and the found CV signals shown in Fig. 4A. The anodic peak response linearly grows with increasing the scan rate from 20 to 200 mV/s. The linear relationship between the anodic peak response and scan rate was derived as $I_{pa} = 0.1655 + 0.0027$ and $R^2 = 0.9978$ and the linear plot displayed in Fig. 4B. From the correlation coefficient ($R^2 = 0.9978$) of linear fitting

equation, the electrocatalytic oxidation Hz was a diffusion-controlled process. The observed slope value is nearly equal to one and evidently proves the electron transfer reactions during the catalytic determination of Hz [34,35].

3.3. Effects of pH.

The effect of pH of the electrolyte solution plays an energetic role in the electrochemical determination of drugs and biological compounds. The pH of the electrolyte directly affects the peak current as well as peak potential of the reporting analyte. The pH effect evaluated using AgNWs/GCE at 50 mV/s scan rate with presence of 250 μ M Hz in the range between 3.0 to 11.0 in 0.05M PBS and the found anodic current results depicted in Fig. 4C. While the pH of the electrolyte solution increases, the anodic peak response increases gradually from 3.0-7.0 after that the peak current decreases. Moreover, the combined plot diagram for the pH vs oxidation peak current and anodic peak potential displayed in Fig. 4D. The maximum oxidation response attained at pH 7.0 for HZ determination while pH 7.0 was selected as the optimal pH of the electrolyte solution for all electrochemical experiments. Moreover, the electrochemical oxidation mechanism of Hz goes through an equal number of proton-electron process [35] and the mechanism displayed in scheme.2.

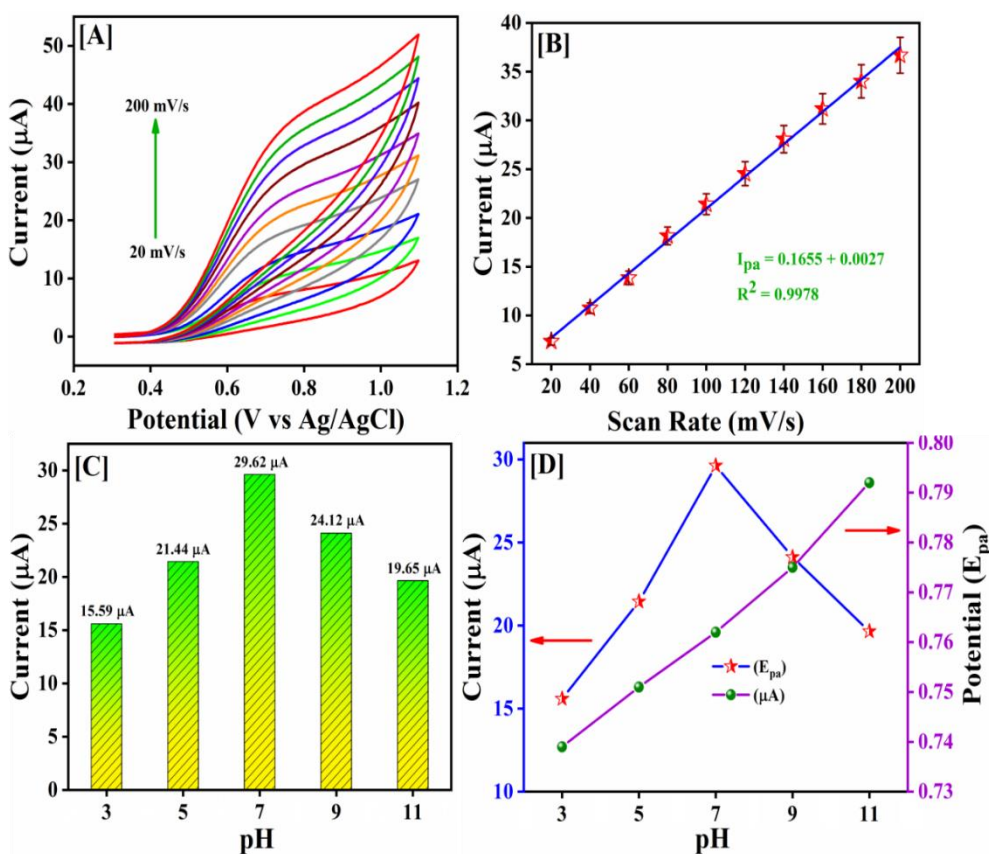
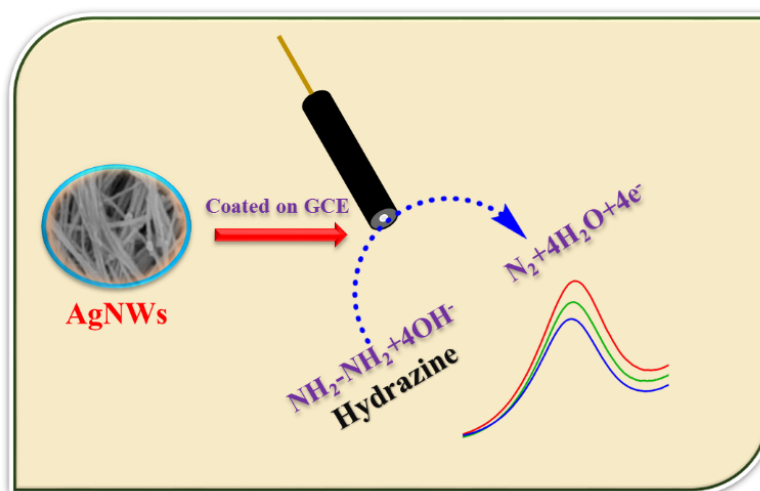


Figure 4. [A] CV signals of various sweep rates from 20-200 mV/s for Hz oxidation on AgNWs/GCE, [B] linear plot for various sweep rates vs. anodic oxidation current, [C] bar graph of anodic peak response against various pH, [D] combine plot illustration for the pH vs oxidation peak response (Blue color) and pH vs anodic peak potential (Violet color).



Scheme 2. Electrochemical Oxidation of Hydrazine at AgNWs/GCE

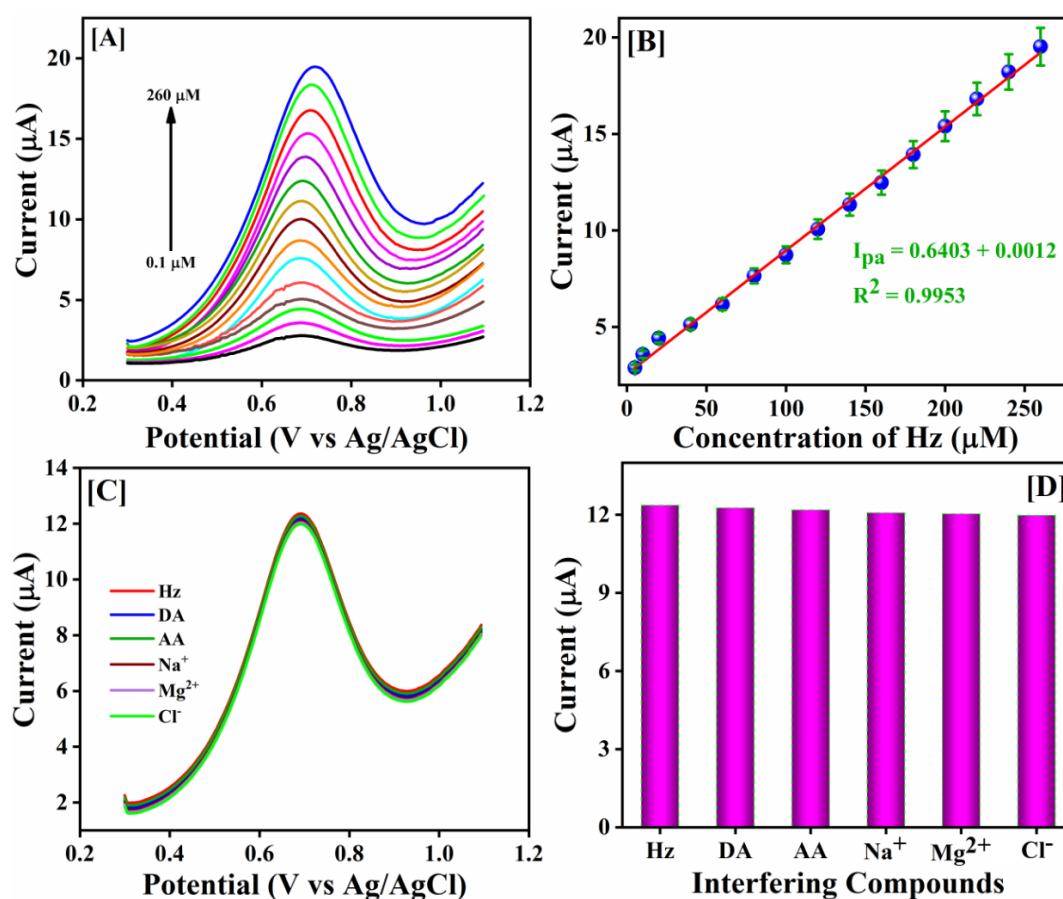


Figure 5. [A] DPV signals at AgNWs/GCE with consecutive addition of Hz from 0.01 - 260 μM , [B] Corresponding linear plot between Hz concentration and oxidation current, [C] CV signals for Hz oxidation with Co-interfering compounds DA, AA, Na^+ , Mg^{2+} , Cl^- , [D] Corresponding bar chart for interfering compounds vs oxidation peak current.

3.4. Electrocatalytic Determination of Hz

The electrochemical determination of AgNWs/GCE of Hz in 0.05M PBS (pH = 7.0) was scrutinized with help of differential pulse voltammetry (DPV) and the found DPV signals displayed in Fig. 5A. From the Fig 5A it was observed that the anodic peak current (I_{pa}) were linearly increasing by increasing the concentration by adding from 0.1 μM to 260 μM of Hz. A distinct and sharp oxidation current observed for each addition of Hz. The electrocatalytic oxidation of Hz was linearly increased and the linear regression equation can be expressed as $I_{pa} = 0.6403 + 0.0012$ and $R^2 = 0.9953$. The electrocatalytic detection parameters like the limit of detection and wide linear range are calculated to be 0.06 μM and 0.01 - 260 μM using ($S/N = 3$) [37]. The electrochemical performance of AgNWs/GCE compared with various modified electrodes tabulated in Table 1. While compared with other modified electrodes the AgNWs/GCE exhibits a low detection limit with a wide linear response range and superior sensitivity. The developed AgNWs via simple sustainable polyol method. The nanowires of Ag deliver superior electrical surface and large active sites which greatly enhance the electron transfer during the oxidation of Hz. These properties enhance the real-time monitoring of Hz and confirm the proposed sensor has a huge benefit from these considerable features.

3.5. Selectivity, Reproducibility and Storage Stability studies

The Selectivity and anti-interfering ability are significant parameters for the proposed sensor devices. To explore the selectivity properties of AgNWs modified GCE with help of DPV was analyzed. The DPV experiment scrutinizing with sweeping amplitude of 50 mV/s in 0.05M PBS (pH = 7.0) in presence of 150 μM Hz with other interfering compounds. Some metal ions and biological compounds are used as interfering compounds such as Na^+ , Mg^{2+} and Cl^- , ascorbic acid (AA), Dopamine (DA).

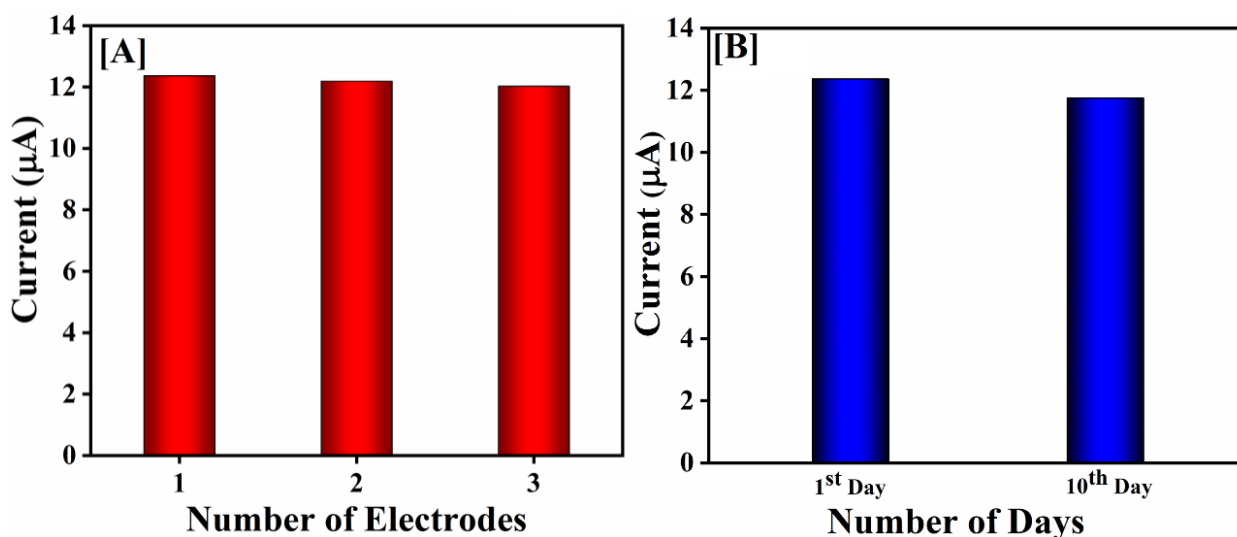


Figure 6. [A] Reproducibility tests for three AgNWs/GCE modified electrodes [B] Stability of the AgNWs/GCE between 1st and after 10 days.

Consequently, 10-fold excess concentration of metal ions and biomolecules were present into the 150 μM Hz and authentic DPV signals displayed in Fig. 5C. Fascinatingly, formerly stated interfering compounds display irrelevant peak response consequences inferior with the Hz oxidation current response. This investigation, clearly exposed that the AgNWs/GCE embraces acceptable anti-interference ability towards Hz determination. In addition, the corresponding bar chart for co-interfering compounds against anodic peak current displayed in Fig. 5D

The reproducibility of the proposed sensor was analyzed with help of DPV with 150 μM consecutive addition of Hz in 0.05 M PBS (pH =7.0) with three various AgNWs/GCE and the observed results depicted in Fig. 6A. All the three modified electrodes response in the same oxidation current towards Hz reveals the superior reproducibility of the proposed sensor. Moreover, the storage capability of the AgNWs/GCE sensor was examined with oxidation peak response of Hz completed with time intervals of 10 days. A 98.5% of its original current response attained for Hz suggest the AgNWs modified GCE has extraordinary storage capability. These observed results show the AgNWs/GCE has outstanding storage capability, satisfactory reproducibility, and accurate sensor towards Hz sensor.

Table 1. Comparison table for the electrochemical oxidation Hz with various modified electrodes

Modified electrode	Technique	Linear range (μM)	LOD (μM)	References
GCE/MWCNT@EA	Amperometric i-t curve	500–9000	0.86	38
GCE/GMC@pep	Cyclic Voltammetry chronoamperometry	70–7000 30 -5000	40 0.5	39
SC/Poly-Tannic acid	Cyclic Voltammetry	0–100	0.1	40
β -nickel hydroxide nanoplatelets/CPE	amperometry	1-1300	0.28	41
GCE/CNT*NiHCF	Amperometric i-t curve	20–200	0.8	42
AgNWs/GCE	DPV	0.01-260	0.06	This work

4. CONCLUSION

We have successfully synthesized uniform silver nanowires (AgNWs) by the polyol method using ethylene glycol as a reducing agent. The polyol method synthesized AgNWs were well characterized using XRD, UV-Visible/NIR and SEM and the observed results confirms the formation of AgNWs without any filths. The prepared silver nanowires showed enhanced electrocatalytic activity towards the electrochemical oxidation of hydrazine. The excellent electrocatalytic ability of the modified electrode AgNWs towards the oxidation of hydrazine with lower potential. The CV responses of AgNWs modified electrode reveals silver electrochemically active which enhances the oxidation process. Since AgNWs exhibit an enhanced catalytic oxidation behavior, we decided to proceed with DPV studies using

the AgNWs modified GCE to achieve lower detection limit with high sensitivity. The linear range for determination of hydrazine was found to be 0.01 - 260 μM and 0.06 μM respectively calculated with help of DPV methods. Therefore, further advantages including outstanding selectivity, superior reproducibility and good stability of the developed method deliver significant response toward real-time sensing of hydrazine.

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