Phosphate-mediated Silver Nanodentrites Modified Glassy Carbon Electrode for the Determination of Nitrophenol

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We present the simple electrochemical fabrication of silver nanodendrites (AgNDs) modified glassy carbon electrode (GCE) for the sensitive determination of nitrophenol (NP) through linear sweep voltammetry (LSV). The surface morphology and elemental composition of the prepared AgNDs were investigated using FESEM (Field Emission Scanning Electron Microscopy), EDX (Electron Diffraction X-ray spectroscopy) and XRD (X-ray diffraction) spectroscopic techniques. The calculated electroanalytical parameters in terms of linear range (20–1380 μM), limits of detection (1.76 μM) and sensitivity (1970 μA mM^{-1} cm^{-2}) evidence the excellent electrocatalytic activity of AgNDs/GCE towards NP determination. The fabricated AgNDs modified electrode possess good selectivity for the detection of NP among other interfering agents. Our constructed LSV sensor for the determination of NP additionally displays appreciable stability and reproducibility.

1. INTRODUCTION

Nitro phenols and their derivatives are categorized as pollutants with high toxicity by world health organization (WHO) and United States environmental protective agency (USEPA)[1, 2]. In particular, 4-nitrophenol (NP) has been characterized in the list of acute carcinogens and mutagens[3]. In spite of its use in pharmaceutical and pesticide industries, the inhalation of NP can lead to cyanosis, drowsiness, headaches as well as nausea in humans[4, 5]. Several analytical methods namely,

electrophoresis[6], gas chromatography[7], spectrophotometry[8], fluorescence[9] and high performance liquid chromatography[10] have been developed for the determination of NP. These methods suffer certain drawbacks like difficult operating procedure, high cost and poor repeatability and reproducibility[11]. To overcome the above mentioned shortcomings, recent researchers prefer the electrochemical methods possessing simple protocol, low cost, high selectivity and good reproducibility for NP determination[12].

Several chemically modified electrodes based on metal and metal oxide nanomaterials, carbon materials as well as conducting polymers have been employed in electrochemical methods to overcome high over potential, poor electron transfers and fouling of unmodified electrodes[13-16]. Among the various above mentioned modifiers, noble metal nanomaterials have been widely utilized in the areas of pharmaceuticals, electronics, environmental analysis, cosmetics and catalysis etc.,[17, 18]. These nanomaterials are highly reactive with adjustable optical properties and high surface to volume ratio. Owing to the superior antibacterial activity along with unique catalytic, electrical, optical, physical and chemical properties, silver nanomaterials are particularly more desirable in various fields (electrochemical sensors and biosensors, food preservation, bio-imaging, antibacterial and photovoltaic materials etc.,) by the current researchers[19-23].

In this work, we have synthesized silver nanodendrites through simple electrochemical deposition and developed a linear sweep voltammetric sensor for the sensitive detection of nitrophenol. The electroanalytical performance of our sensor in terms of linear range (20–1380 μM), limits of detection (1.76 μM) and sensitivity (1970 $\mu A \ mM^{-1} \ cm^{-2}$) were quite adequate. The high sensitivity and selectivity towards the determination of nitrophenol reveals the good electrocatalytic activity of the modified fabricated electrode.

2. EXPERIMENTAL

2.1 Reagents

Silver nitrate ($AgNO_3$), Sodium phosphate dibasic (Na_2HPO_4), Sodium dihydrogen phosphate (NaH_2PO_4), and Nitrophenol ($C_6H_5NO_3$) were purchased at an analytical grade from Sigma-Aldrich. Sodium phosphate dibasic (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) were used to prepare 0.05 M phosphate buffer (PB) solution and the pH was adjusted to 5 by adding few drops of concentrated sulphuric acid. This 0.05 M PBS (pH 5) was utilized as the supporting electrolyte for all the electrochemical experiments. Prior to each experiment, all the solutions were deoxygenated with pre-purified N_2 gas for 15 min unless otherwise specified. The entire electrochemical studies were done using double distilled water (conductivity $\geq 18 \ M\Omega \ cm$).

2.2 Apparatus

CHI 6171D work station in a conventional three electrode system was employed to perform the electrochemical experiments including linear sweep voltammetry (LSV). This system uses modified

GCE (area 0.071 cm^2) as working electrode, saturated Ag|AgCl (saturated KCl) as reference electrode and Pt wire as counter electrode. The analysis of morphology and elemental composition was carried out using Field emission scanning electron microscopy (FESEM, Hitachi S4700) and energy dispersive X-ray (EDX, HORIBA EMAX X-ACT).

2.3 Fabrication of AgNDs nanocomposite modified GCE

The electrode surface of GCE (glassy carbon electrode) was polished with a Buehler polishing kit using 0.05 μm alumina slurry followed by washing with double distilled water and ethanol. AgNDs was electrochemically prepared by following the earlier reported procedure. Typically, silver nitrate (5 mM) and hydrogen phosphate anions (10 mM) were mixed together and agitated to form Ag_3PO_4 (yellow coloured silver phosphate precipitate). Later, the addition of 0.05 M ammonium hydroxide (NH_4OH) solution changes the intense yellow Ag_3PO_4 precipitate in to $Ag[(NH_3)_2] PO_3^-$ (colourless solution of silver-ammine complex). This resulting solution was further employed as the electrolyte for the deposition (200 s) of AgNDs at -1.1V (Ag|AgCl).

3. RESULT AND DISCUSSION

3.1 The study of surface morphology
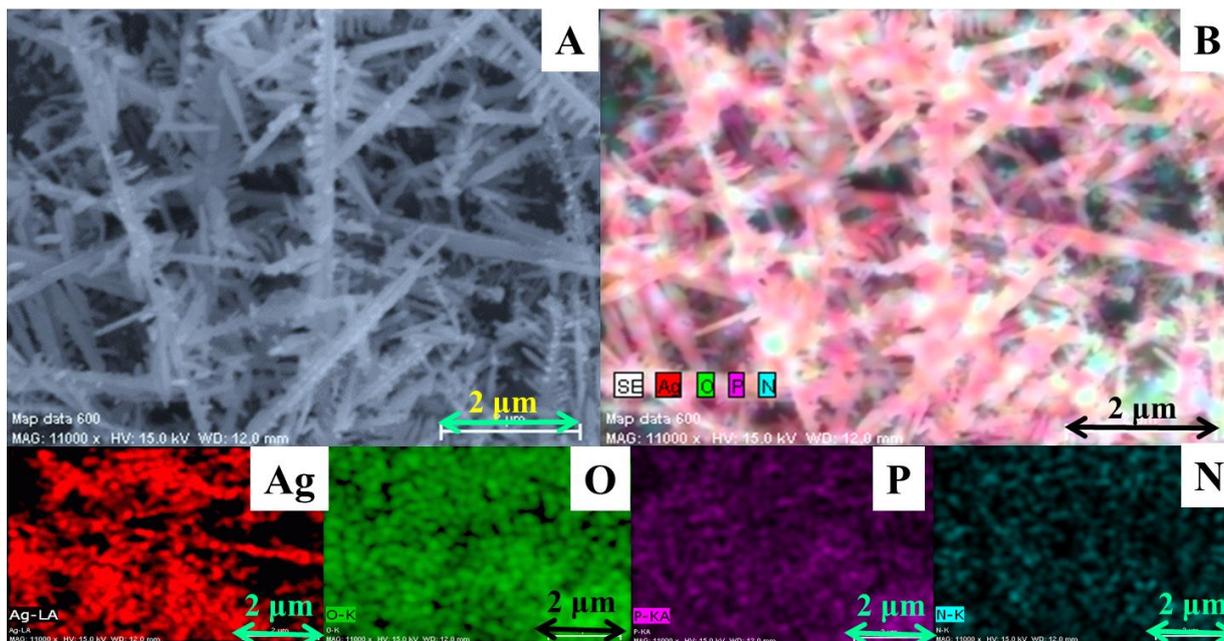
Figure 1. (A) SEM image of AgNDs. (B) Elemental mapping of AgNDs (Ag, O, P and N)

The surface morphology of the prepared silver nanodentrites was studied using field emission scanning electron microscopy (FESEM) and the images are presented in **Figure 1A**. This FESEM

image describes the dendritic morphology of electrochemically deposited silver with well grown main and side branches. **Figure 1B** displays the energy dispersive X-ray (EDX) spectrum of the deposited silver nanodendrites. From the elemental analysis using EDX spectroscopy, the weight percentages of the elements present (silver, oxygen, phosphorous, and nitrogen) were confirmed. The higher mapping of oxygen can be due to the signal from oxygen present in indium tin oxide plate. The prepared AgNDs contains substantial weight percentages of silver, phosphorous and nitrogen. It was revealed from the corresponding EDX images. The XRD pattern of the as deposited AgNDs has been exhibited in **Figure 2**. The obtained diffraction peaks at the 2θ values of 38°, 44.2°, 64.5° and 78° represents (111), (200), (220) and (311) crystal planes of metallic silver. These above mentioned diffraction peaks are in concordance with the formerly reported major diffraction peaks of silver in the literatures[24].
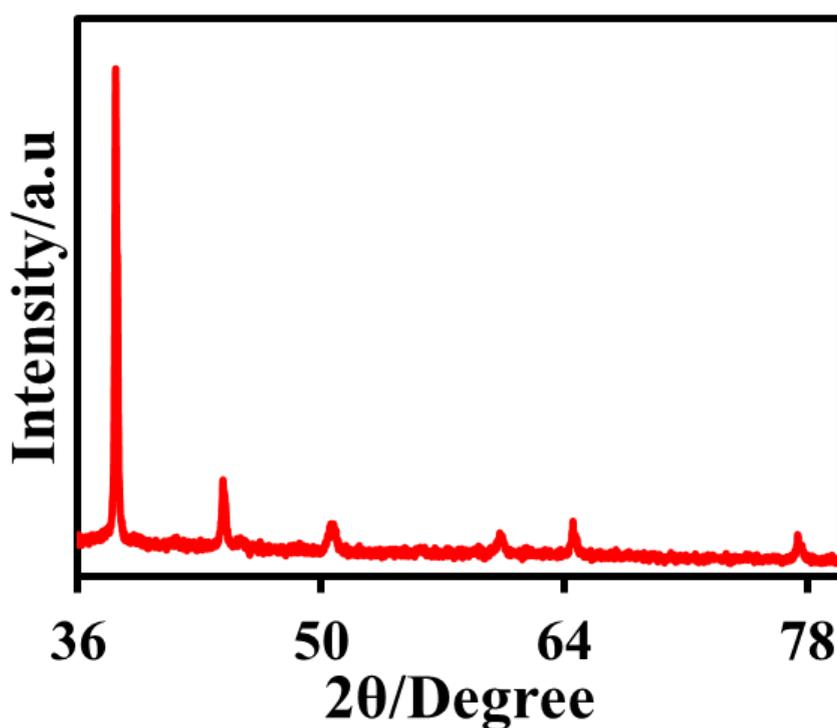

Figure 2. X-ray diffraction pattern of AgNDs

3.2 Determination of NP: Cyclic voltammetry

The electrochemical performance of unmodified and AgNDs modified GCE towards 0.5 mM NP in 0.05 M PBS (pH 5) at the scan rate of 50 mV/s was shown in **Figure 3**. As can be seen in the figure, AgNDs/GCE displayed an enhanced peak current response at -0.3 V (vs. Ag|AgCl) compared to the feeble peak response of unmodified GCE towards 0.5 mM NP. Relative to unmodified GCE, several folds higher current response observed at AgNDs modified GCE. Thus, the excellent catalytic activity of AgNDs in the determination of NP was revealed from the good conductivity and biocompatible nature of AgNDs. Additionally, we have given the possible electron transfer processes involved in 4-NP at AgNDs/GCE in **Scheme 2** [17].
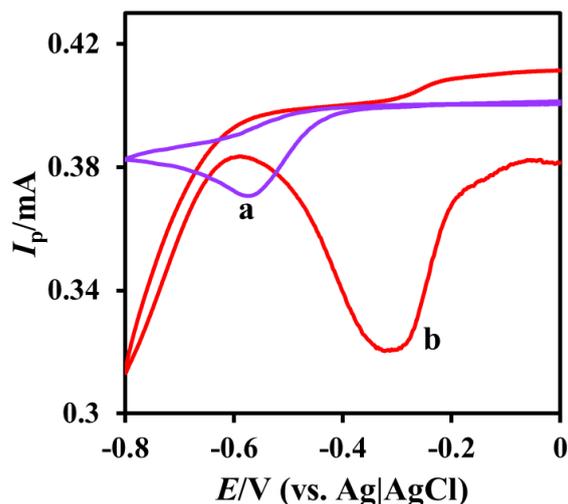
Figure 3. CVs observed at (a) unmodified and (b) AgNDs modified GCE in the presence of 1 mM hydrazine (electrolyte = 0.05 M PBS (pH 5))
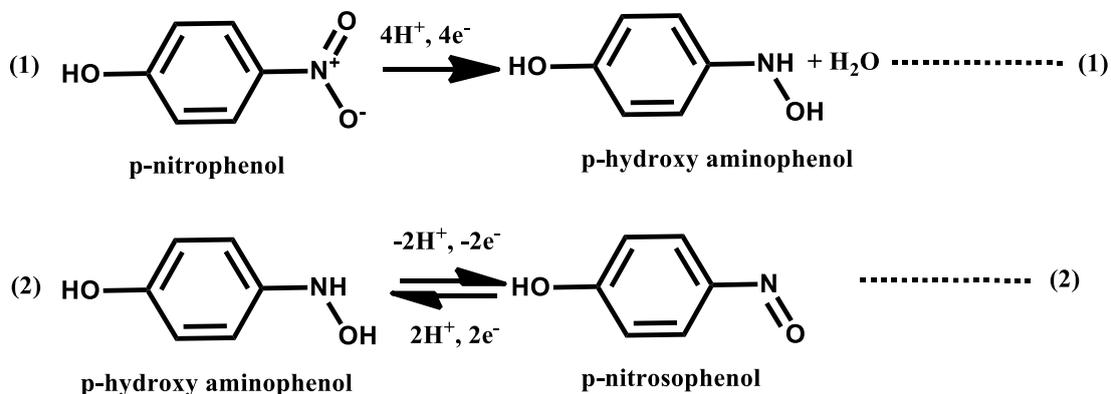

Scheme 2. Schematic representation of electron transfer processes involved in 4-NP at AgNDs/GCE

3.3 Effect of Concentration

Cyclic voltammetry was employed to study the effect of NP concentration at AgNDs/GCE in 0.05 M PBS (pH 5) at the scan rate of 50 mV/s. The corresponding cyclic voltammograms were displayed in **Figure 4A**. No noticeable peak current response (curve a) was appeared in the absence of NP, exposing the electro inactive behavior of AgNDs/GCE. On the other hand, a well-defined cathodic peak response (curves b to m) was shown by our fabricated electrode towards each addition of 0.25 mM NP. The linearity between [NP] and I_p was shown in **Figure 4B**. A linear increase in the cathodic peak current response observed for the increasing concentration of NP, indicates the good electrocatalytic ability of AgNDs/GCE in the determination of NP.
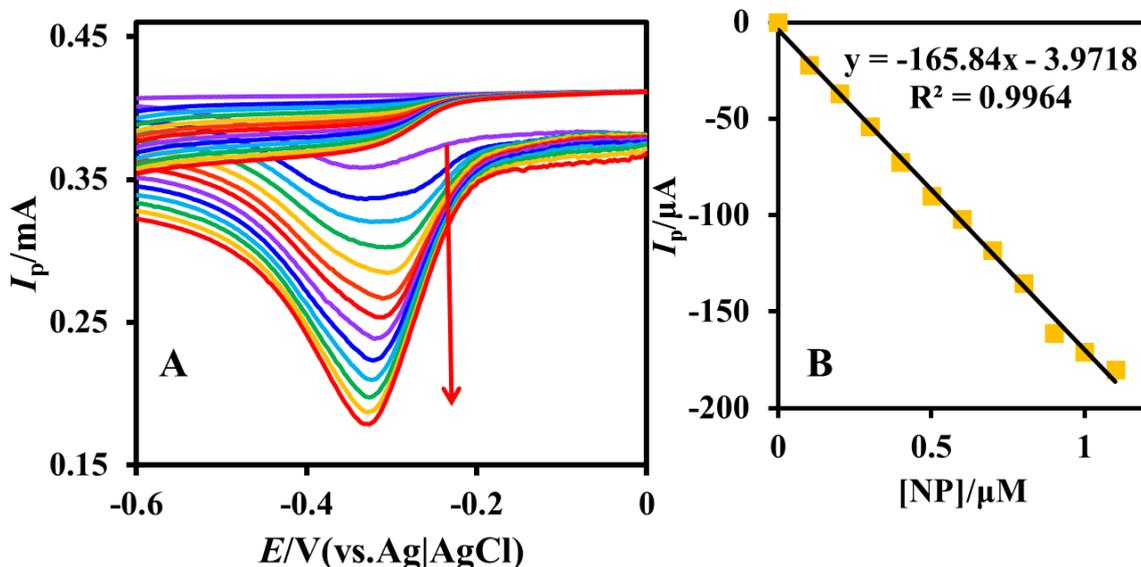
Figure 4. (A) CVs obtained at AgNDs/GCE in the absence (a) and presence (b-m) of NP (each addition of 0.25 mM) in 0.05 M PBS (pH 5) at the scan rate of 50 mV/s. (B) Calibration plot between [NP] and I_p
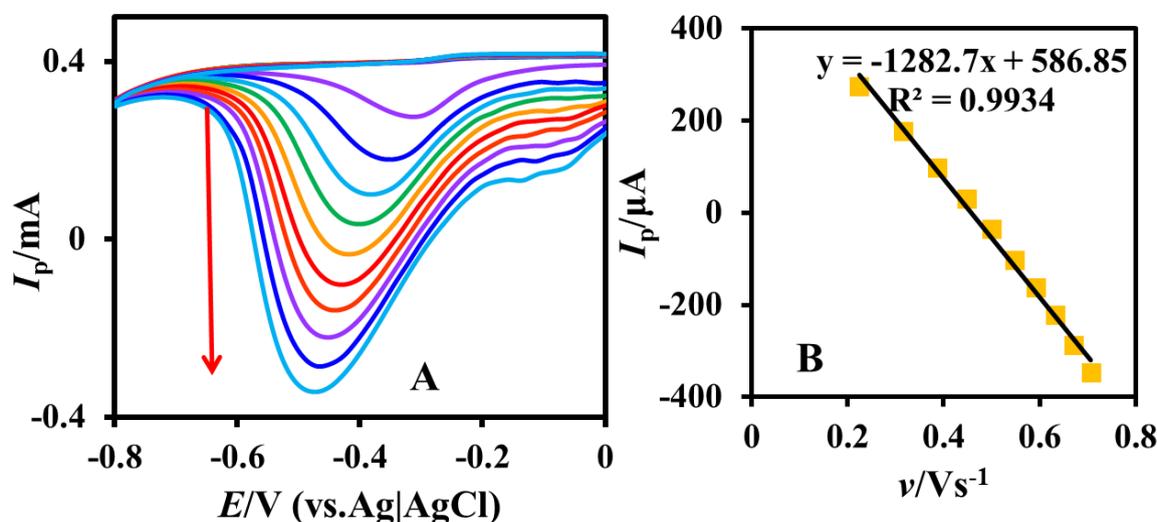

Figure 5. (A) CVs for varying scan rate (0.05 to 0.5 V/s) at AgNDs/GCE in 0.05 M PBS (pH 5) containing 1 mM NP. (B) Calibration plot for $v^{1/2}$ vs I_p

3.4 Effect of Scan rate

The influence of scan rate at AgNDs/GCE in 0.05 M PBS (pH 5) was investigated using cyclic voltammetry (**Figure 5A**). The fixed concentration of NP was 1 mM. The increasing scan rate from 0.05 to 0.5 V/s resulted in the linear increase of cathodic peak current response at AgNDs/GCE for the determination of NP. The shift of oxidation peak potential towards the positive direction was also observed. The calibration plot in **Figure 5B** reveals the linear relationship between cathodic peak current response and square root of scan rate, which in turn supports the good electrocatalytic activity of towards NP[17].

3.5 Electrochemical determination of NP: Linear sweep voltammetry (LSV)
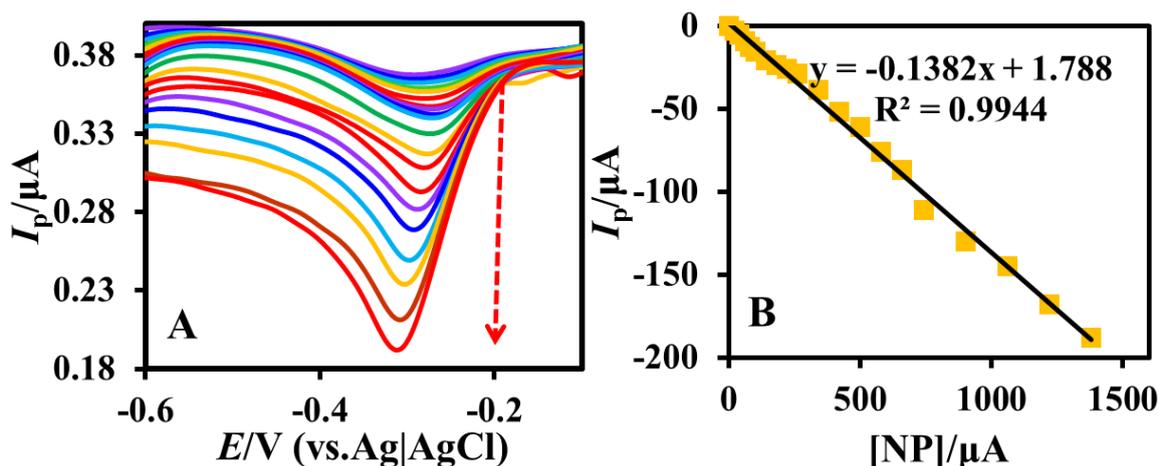
Figure 6. (A) LSVs at AgNDs/GCE for varying concentrations of NP (0 μM to 1500 μM) in 0.05 M
PBS (pH 5) at the fixed scan rate of 50 mV s^{-1}. (B) Calibration plot between I_p vs [NP]/μM

Table 1. Comparison of AgNDs/GCE performance towards NP determination with other various
modified electrodes

Modified Electrode	Linear range (μM)	[a]LOD (μM)	Sensitivity	Reference
[b]Ag-NPs	0.1–350	0.015	2.57 μA μM^{-1} cm^{-2}	[17]
[c]GO/GCE	0.1–120	0.02	–	[25]
[d]AgNWs–[e]PANI	–	0.052	–	[26]
GR/[f]MIPs	0.01–100,200–1000	0.005	–	[27]
[g]PDDA-GR	0.06–2, 10–110	0.02	–	[28]
[h]NMP/GR	0.50–5.60	0.15	28.84 μA/μmol L^{-1}	[29]
GR	50 to 800	42	–	[30]
[i]tmaePcCo/[j]CNT	1.0 – 1800	0.2	102.61 μA mM^{-1}	[31]
[k]PMO	0.6 to 12	0.11	–	[32]
[l]pDAT–GR	5–1500	0.037	0.7113 μA μM^{-1}	[33]
AgNDs/GCE	20–1380	1.76	1970 μA mM^{-1} cm^{-2}	This work

[a]LOD –limits of detections, [b]Ag-NPs–Silver nanoparticles, [c]GO– Graphene oxide, [d]AgNWs–silver
nanowires, [e]PANI–Poly aniline, [f]MIPs– molecularly imprinted polymers, [g]PDDA–
poly(diallyldimethylammonium chloride), [h]NMP– N-Methylphenazonium methyl sulfate, [i]tmaePcCo–
cationic tetra-β-(N,N,N-trimethylaminoethoxy) phthalocyaninecobalt(II), [j]CNT–Carbon nanotubes,
[k]PMO– poly(methyl orange), [l]pDAT– polymerized 3,5-diamino-1,2,4-triazole.

    Figure 6A presents the linear sweep voltammograms towards the electro oxidation of NP at
AgNDs/GCE in 0.05 M PBS (pH 5). The fixed values of scan rate (50 mV/s) and potential range (-
0.2V to -0.6V) were applied for this study. The various concentrations of NP chosen to perform this
technique are: 20, 40, 80 and 160 μM of NP. The cathodic peak current response for the determination
of NP showed a linear increase from 20 to 1380 μM. The values for limits of detection (LOD = 1.76

µM) and sensitivity (1970 µA mM^{-1} cm^{-2}) were evaluated from the calibration plot between concentration of NP and the corresponding peak current response (**Figure 6B**). The biocompatible nature and high conductivity of silver led to the excellent electro oxidation of NP at AgNDs/GCE. The electroanalytical parameters such as linear range, LOD and sensitivity of our fabricated electrode were in concordance with the electroanalytical parameters of the earlier reported NP sensors (**Table 1**).

3.6 Selectivity studies

The selective nature of AgNDs/GCE towards NP in presence of other interferents was also studied. The chosen interfering compounds such as Catechol, Resorcinol, Hydroquinone, dopamine, uric acid, glucose, p-Nitrobenzoic acid, p-Nitrobenzyl alcohol and m-Acetamidophenol were in 100 folds excess concentration than that of NP (50 µM). The presence of biomolecules and phenol derivatives showed a less effect (4%) on the peak response of NP. However, the strong influence of interfering nitro compounds (8%) and very less effect of common metal ions (3%) were observed on the response current given by NP. This is because of the oxidation of nitro groups in the interferents occurring at the same potential optimized for the electro oxidation of NP. In the presence of common metal ions and biomolecules, AgNDs/GCE can detect NP with high selectivity.

3.7 Stability, Repeatability and Reproducibility

The fabricated electrode was stored in 0.05 M PBS (pH 5) at 4 °C and the cathodic peak current response was recorded every day towards 1 mM NP for 30 days. 95.3% of the initial response current was recovered as the final response current. This showed the appreciable stability of AgNDs/GCE. The relative standard deviation (RSD) value for the considerable repeatability nature of AgNDs/GCE was found to be 2.6 % by utilizing 5 independent modified electrodes. The acceptable reproducing capability of our sensor was evident from the RSD value 3.1% calculated based on the determination of NP using single fabricated electrode.

3.8 Real sample analysis

Table 2. Determination of NP at AgNDs/GCE in various tap, river and lake water samples

Samples	Added (µM)	Found (µM)		Recovery values (%)
		Proposed method	**HPLC method**	
Tap water	50	50.6	50.2	101.2
	100	99.3	99.9	99.3
River water	50	49.63	49.87	99.26
	100	99.23	99.63	99.23
Lake water	50	50.3	49.6	100.6
	100	99.81	99.6	99.81

LSV technique was employed to check the practical feasibility of AgNDs modified GCE towards the determination of NP. Three different water samples namely, tap water, river water and lake water were taken for the examination based on standard addition method. The recovery values evaluated for the spiked concentrations of NP in the water samples were found to be quite satisfactory. The calculated recovery values were compared with the acquired values from HPLC method and presented in **Table 2**. Thus, the better feasible practicality of AgNDs/GCE was evident from the NP analysis in real samples.

4. CONCLUSIONS

In brief, the successful construction of a linear sweep voltammetric sensor has been done using electrochemically prepared AgNDs. CV, FESEM, EDX and LSV techniques were employed to characterize the as-synthesized AgNDs. The electrochemical behavior of AgNDs/GCE was active in the potential range from 20 to 1380 μM. The AgNDs modified glassy carbon electrode can selectively detect NP with low limit of detection (1.76 μM) and high sensitivity (1970 $\mu A\ mM^{-1}\ cm^{-2}$) in presence of other interferents. Our fabricated electrode also possess good stability, considerable repeatability and acceptable reproducibility towards NP. AgNDs/GCE holds extensive applications (batteries, biosensors and optics) in near-future because of its simple operations steps, low cost as well as excellent electrocatalytic ability in the determination of NP.

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