Electrochemical detection of nitrite using glassy carbon electrode modified with silver nanospheres (AgNS) obtained by green synthesis using pre-hydrolysed liquor

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Abstract: Silver nanospheres (AgNS) with SPR band ~417 nm was synthesized by Green synthesis, using a pre-hydrolysed liquor (PHL) of *Nilgiri* wood without any pretreatment. The synthesis was carried out at room temperature and was complete within three hours. The reduction and stabilization of silver is brought about by hemicelluloses present in the pre-hydrolysed liquor. Electrochemical oxidation of nitrite on glassy carbon electrode (GCE) modified with the AgNS in 0.1 M phosphate buffer solution (PBS) of pH 7.0 was found to occur at 0.86 V with respect to Ag/AgCl. Electrochemical sensing experiments with AgNS/GCE showed a linear range of detection between 0.1 to 8 μM, with detection limit of 0.031 μM and a sensitivity of 580 μA mM^{-1}cm^{-2}.

Keywords: Electrochemical sensor · Silver nanospheres · Nitrite · Green synthesis · pre-hydrolysed liquor

1. Introduction

Owing to the unique advantages of electrochemical techniques, electrochemical detection of inorganic pollutants such as nitrite has received significant attention in the recent era. Nitrite contamination in natural water, soil and food [1,2] and subsequently in human beings and animals results from its extensive utilization as an additive, preservative in food industries, fertilizer and as corrosion inhibitor [3–6]. Nitrite, also formed by the conversion of nitrate in the saliva pose serious problem to human health [7, 8]. It affects the normal functioning of the hemoglobin i.e., carrying oxygen in blood to other parts of the body, and at higher levels leads to methemoglobinemia commonly known as "blue baby syndrome" in babies [9–11]. When severe and untreated, causes brain damage and eventually results in death due to lack of oxygen [12]. Therefore, there is a great demand for easy and effective methods for monitoring low levels of pollutants such as nitrites and also for their removal [13, 14]. Electrochemical techniques such as amperometry and differential pulse voltammetry can be seen as a highly sensitive, selective and facile methods for electrochemical sensing. Being environmentally benign and economical, electrochemical methods of nitrite detection outperform among different methods including chromatography [15], spectrophotometry [16], chemiluminescence [17], spectrofluorimetry [18] and flow injection analysis [19] that are expensive and time consuming.

A major challenge to the researchers in this field is to reduce the over potential associated with the electrochemical reaction and to increase the sensitivity, for which metal nanoparticles come as a rescue. A number of metal nanoparticles based systems not restricted to the below have been explored to achieve the required analytical performance. Electrodes based on poly(2-aminothiophe-nol) modified with Pt nanoparticles developed for electrochemical sensing of nitrite in food samples is reported by M S Tehrani et al [20]. Gold nanoparticles incorporated zinc based metal-organic frame work is reported by D K Yadav et al for selective recognition of nitrite [21]. Palladium nanoparticles supported on graphite obtained via microwave synthesis and used for detection of nitrite in lake water and sausage samples is reported by Jing-He Yang et al [22]. Au@Fe$_2$O$_3$ immobilized on L-cysteine modified glassy carbon electrode was developed by C Yu et al which showed high electrocatalytic activity to nitrite oxidation [23]. However, electrodes based on silver nanoparticles (AgNPs) possess advantages in the form of high conductivity (highest among the noble metals) and associated low cost. And, it is very obvious that the catalytic activity of any material largely depend on the surface area and adsorption characteristics that in turn depend on the method of preparation [24]. Though, there are many synthetic routes developed to produce a range of nano sized silver [25–27], they either employ harsh reaction conditions, toxic reducing agents and organic solvents which are not environmentally benign or result in agglomerated nanoparticles. In addition, conventionally

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synthesized nanoparticles have restricted evaluation in bio-sensing applications, thus making biogenic based principle as an alternative approach for producing nanoparticles. A variety of biomaterials have been shown to be used for the synthesis of nanoparticles. To cite a few, aqueous extract of dried fresh leaves powder of Ferula Latisecta was prepared and treated with silver nitrate at 70 °C, 500 rpm for 48 hours to obtain AgNPs as reported by Z. Rashid et al [28]. P. Logeswari et al [29] have demonstrated the eco-friendly synthesis of silver nanoparticles from commercially available plant powders such as *S. tricobatum*, *S. cumini* and *C. asiatica*, by treating the ethanolic extract of each plant powder with $AgNO_3$ and incubating at 37 °C under agitation (200 rpm) for 24–48 hours. In another study Blackberry, Blueberry, Pomegranate and Turmeric extracts were added to gold or silver salt solutions and left overnight at room temperature under vigorous stirring for completion of the synthesis [30].

In all these studies, it can be observed that firstly constituents of the bio source are suitably extracted by consuming energy and time. The extract is then employed for the synthesis of the nanoparticles that involves long time periods and continuous stirring. The biomolecules present in the extract play the role of reducing and stabilizing agents. However, in the present study, the synthesis of AgNS is brought about using pre-hydrolysed liquor, a waste generated in pulp industry without any further treatment. In the pulp mills, wood chips (*Nilgiri* in the present work) are treated in a high-temperature prehydrolysis step to remove hemicelluloses in the "prehydrolysis kraft dissolving pulp production process". During this procedure, hemicelluloses and other organics are dissolved in the pre-hydrolysed liquor (PHL) [31,32]. The PHL thus contains water soluble metabolites such as reducing sugars along with disaccharides, oligosaccharides and non-saccharides from *Nilgiri* Wood. These metabolites help to reduce the metal ions into metal nanoparticles as well as allow them to be stable even after two months. This paper describes the Green synthesis of AgNS using pre-hydrolysed liquor generated from pulp industry, characterization and their catalytic activity for electrochemical nitrite detection.

2. Experimental

2.1 Chemicals and Reagents

Three batches of pre-hydrolysed liquor of *Nilgiri* wood was collected from pulp industry located in north Karnataka. Sodium nitrite ($NaNO_2$), di-potassium hydrogen phosphate (K_2HPO_4), potassium di-hydrogen phosphate (KH_2PO_4), potassium chloride (KCl), sodium chloride (NaCl), ammonium nitrate (NH_4NO_3), glucose, urea, magnesium nitrate ($Mg(NO_3)_2$), calcium chloride ($CaCl_2$), sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), ammonium chloride (NH_4Cl) (all s.d. fine, India) and silver nitrate ($AgNO_3$) (BDH, India) were of analytical grade and used without any further purification.

0.1 M phosphate buffer solutions (PBS) of different pH were prepared by mixing appropriate amounts of K_2HPO_4 and KH_2PO_4 and were employed as the supporting electrolyte. Double distilled water (DDW) was used for the preparation of all the required solutions.

2.2 Preparation of AgNS

10 mL of diluted pre-hydrolysed liquor from *Nilgiri* wood was added to 50 mL of 1 mM silver nitrate solution and stirred vigorously at ambient temperature. The resulting light yellow coloured solution slowly turned darker and finally attained reddish amber colour around 150 minutes of continuous stirring indicating the formation of AgNS. The formation of AgNS was also monitored on the UV-Vis spectrometer. The synthesized AgNS were collected by high-speed centrifugation (REMI R-24) at 12,000 rpm for 30 minutes. The partially purified AgNS were repeatedly washed with ethanol and distilled water to remove any undesirable components. Finally, AgNS were collected in powder form by drying in hot air oven at 70 °C overnight.

2.3 Characterization

The formation of AgNS was periodically monitored by recording the UV-Vis spectrum of the resulting suspension for SPR on UV-Visible spectrometer (Agilent carry 60) in the wavelength range of $200 - 800$ nm. The powder XRD pattern of AgNS was obtained using 'X'PERT-PRO XRD (PANalytical's X-ray diffractometer) with Cu Kα radiation in step scan mode at scan rate of $2°$ min^{-1} with 2θ ranging from 20 to 80°. The surface morphology of the as synthesized AgNS was obtained by TEM (JEOL, JEM-2100 EX) operated at a voltage of 200 kV. FTIR spectrum of the AgNS was recorded on a FTIR spectrometer (PerkinElmer-L160000 A, USA) with a resolution of 4 cm^{-1}. All the electrochemical experiments were performed using Chi.660E electrochemical work station using three electrode assembly. Bare GCE (3 mm diameter) or AgNS/GCE were used as working electrodes, and platinum wire and Ag/AgCl were used as counter and reference electrodes respectively. All the solutions were deoxygenated before carrying out electrochemical measurements.

2.4 Modification of Electrode

Prior to use, the GCE was cleaned by polishing with 0.3 and 0.05 micron alumina to get a mirror shiny surface, rinsed with doubly distilled water (DDW) and sonicatied for 2 minutes in ethanol and DDW successively. GCE was modified by drop coating 10 μL of a homogeneous suspension containing 5 mg of AgNS, 20 μL of Nafion (as a binder) and 980 μL DDW (optimized condition) and dried at ambient temperature for three hours. The resulting electrode is represented as AgNS/GCE.
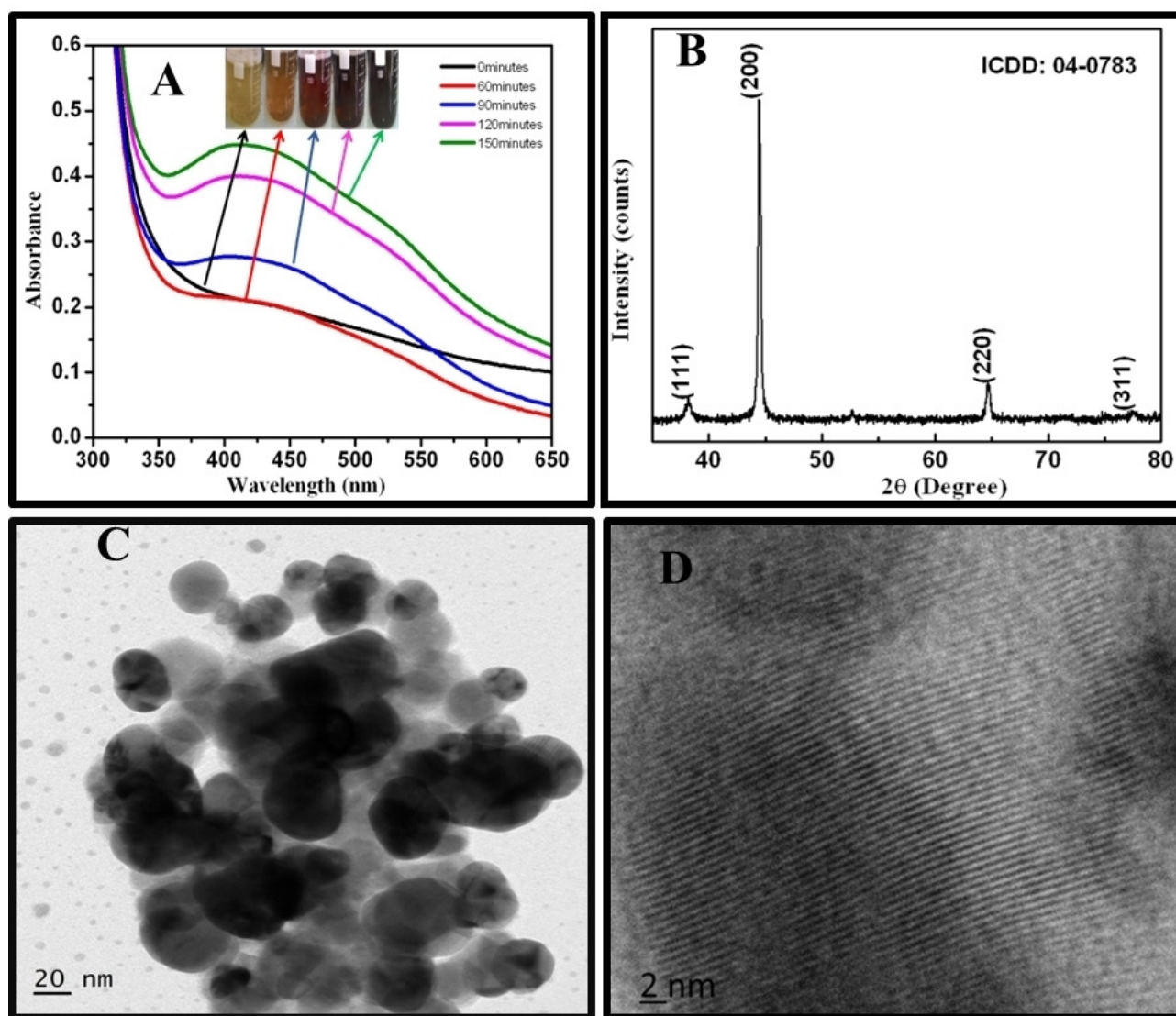
Fig. 1. (A) UV-Vis spectra of the reaction mixture at different time intervals. Inset shows the corresponding colour changes. (B) XRD pattern, (C) and (D) TEM and HRTEM images of AgNS obtained by green synthesis using pre-hydrolysed liquor.

3. Results and Discussion

3.1 Synthesis and Characterization

The formation of silver nanospheres was monitored by surface plasmon resonance (SPR) band in the UV-Vis spectra. Figure 1A shows a broad SPR band with maximum absorption around 417 nm, characteristic of silver nanoparticles that appeared only after one hour of continuous stirring and gradually increased in intensity and get saturated after two and half hours of stirring. Absorption in the region of 520 nm indicate the slight agglomeration of the particles during the synthesis.

In Figure 1B, the XRD pattern of the silver nanospheres is presented. The diffraction peaks at 2θ values of 38.19°, 44.46°, 64.63 ° and 77.34° corresponding to (111), (200), (220) and (311) planes respectively, are attributed to face centered cubic crystalline (FCC) structure of metallic silver. The average crystallite size of the silver nanospheres was calculated from Scherrer equation and was found to be ~30 nm. Figure 1C &D exhibit the morphological analysis of the nanospheres by TEM revealing predominantly spherically shaped nanoparticles with average diameter of ~ 20–30 nm. This control in size of the nanospheres is effectively brought about by the hemicellulose present in the pre-hydrolysed liquor, in addition to reduction of silver ions to silver nanospheres. Though there is minor agglomeration, majority of the particles can be seen individually which will effectively provide large surface area, a prerequisite for any catalytic reaction. Repeated synthesis and characterization of the silver nanospheres from different batches of the pre-hydrolysed liquor demonstrated the reproducibility with the current material and method. The pre-hydrolysed liquor contains xylose and arabinose as major constituents
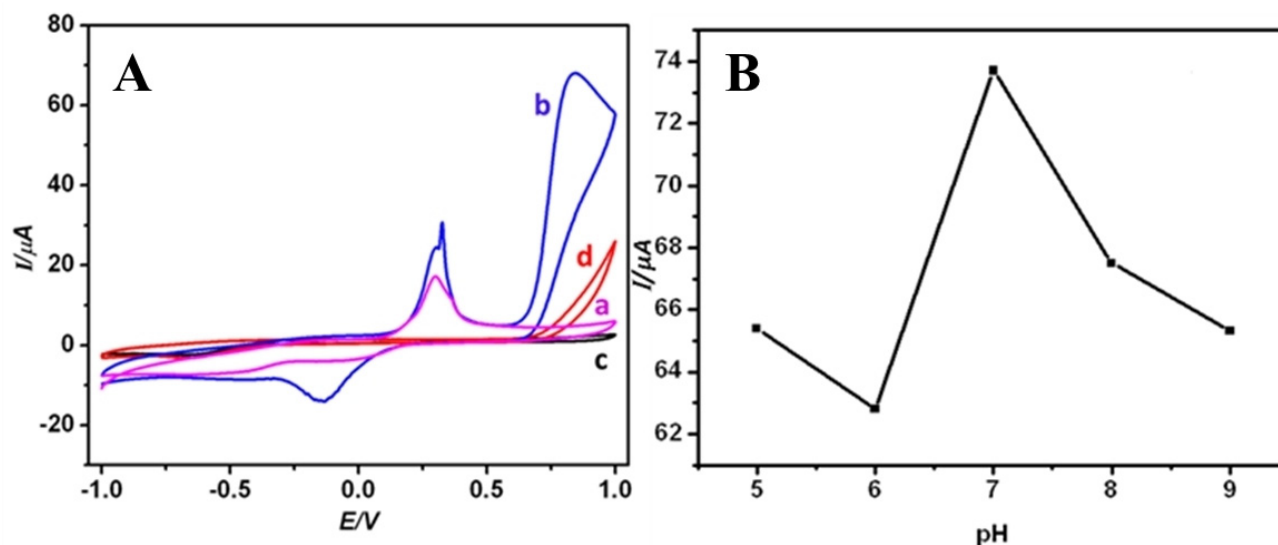
Fig. 2. (A) CVs of AgNS/GCE in absence (curve a) and presence (curve b) and bare GCE in absence (curve c) and presence (curve d) of 3 mM NaNO$_2$. Supporting electrolyte is 0.1 M PBS (pH = 7.0) and the scan rate is 50 mV/s. (B) Effect of solution pH on the oxidation current of 3 mM NaNO$_2$ at AgNS/GCE in 0.1 M PBS obtained from CVs.

and mannose in small amounts as analyzed from the HPLC (RI detector) (Figure S1, supporting information). The silver ions possibly complex with the negatively charged hydroxyl and carboxylate groups in these biomolecules and subsequently get reduced, resulting in the formation of silver nanospheres. FTIR spectrum of the dried AgNS was recorded to identify the possible phytoconstituents present in the pre-hydrolysed liquor that help in the reduction of silver ions and stabilization of AgNS. FTIR spectrum of the as-synthesized AgNS using pre-hydrolysed liquor is shown in Figure S2 of the supporting information. The bands observed at 3439, 1630 and 2924 cm^{-1} can be respectively assigned to –OH stretching of polyphenols that are commonly found in plants, amide C=O stretching in the proteins of the *Nilgiri* wood and aldehydic C–H stretching. The band observed at 1744 cm^{-1} is attributed to the acetyl groups of the hemicelluloses or to the ester linkage of carboxylic stretching group of ferulic acid found in plant cell wall. The bands at 1018 and 1568 cm^{-1} can be assigned to hemiacetal and bending frequency of the secondary amines of proteins respectively. The bands observed at 581 and 660 cm^{-1} corresponds to Ag–O and Ag-OH respectively. Observation of these bands in FTIR spectrum of AgNS clearly indicate the adsorption of some bioactive molecules having reducing functional groups viz., C=C, C=C, (NH)C=O (flavanones, proteins and amino acids), –OH (polyphenols) and hemicelluloses from the PHL on to the AgNS. The presence of these reducing compounds in the PHL brings about the reduction of silver ions and their adsorption on the AgNS preventing their agglomeration [31, 32, 34–36].

3.2 Electrocatalytical Studies

The electrochemical behavior of the silver nanospheres coated on GCE was evaluated by cyclic voltammetry in 0.1 M PBS, pH 7 at 50 mV/s in the potential range of −1 and 1 V. Curve 'a' of Figure 2 A shows the oxidation of silver to occur in the positive scan at +0.28 V followed by its reduction in the negative scan at −0.16 V. Addition of 3 mM NaNO$_2$ (curve 'b', Figure 2A) to the buffer solution resulted first in oxidation of nitrite complexed with silver to NO$_2$ at +0.24 V followed by oxidation of silver at +0.28 V as depicted in equations 1 and 2 respectively. Third oxidation peak in the positive cycle of the voltammogram observed at +0.86 V appeared due to the irreversible oxidation of the NO$_2$ to nitrate ion as represented in equation 3 [37,38]. The potential at which the nitrate ion formation is electrocatalyzed by the silver nanospheres is lower compared to other materials especially the silver prepared by bio mediation [21, 22]. The catalytic property of the silver nanospheres is also evidenced from the pronounced oxidation current for nitrite oxidation. In the reverse scan, the currents for the reduction of silver and formation of HNO$_2^-$ as given in equations 4 and 5 respectively are observed at −0.16 V and around −0.35 V [4, 5, 33]. Bare glassy carbon in the same solutions showed inert response in the potential ranges studied (curves "c" and "d" in Figure 2A). These results clearly demonstrate the electrocatalytic properties of the silver nanospheres prepared using pre-hydrolysed liquor towards nitrite oxidation and hence can be employed for nitrite sensing. The probable electrooxidation mechanism of nitrite on AgNS is proposed according to equations (1) to (5) based on the literature reports [33].
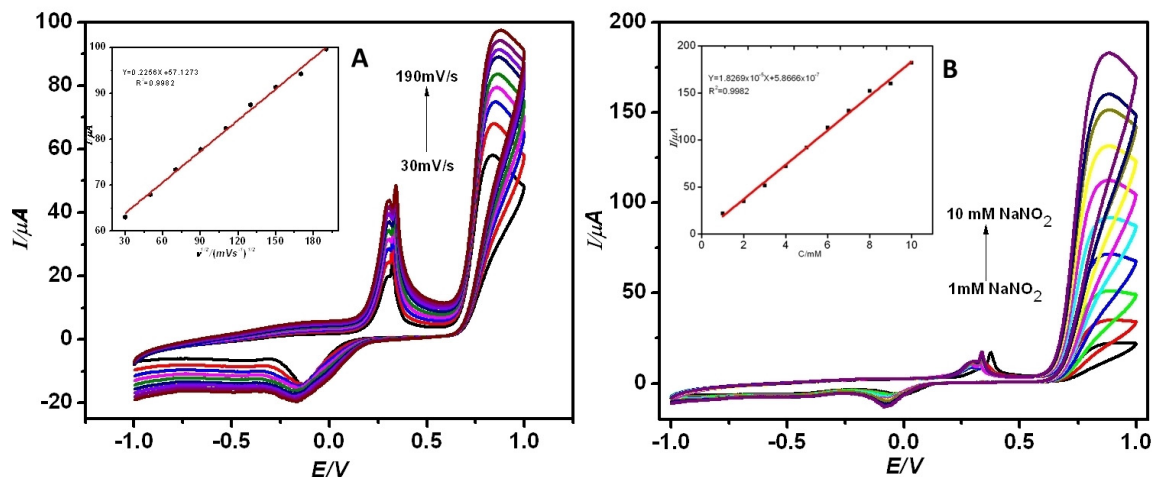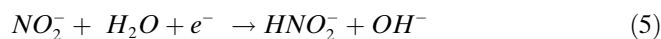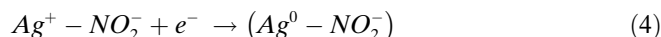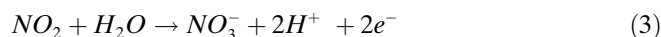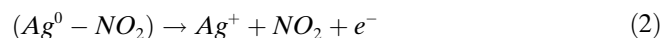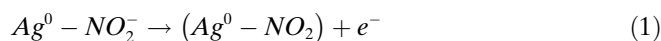
Fig. 3. A) CV responses of AgNS/GCE in the presence of 3 mM NaNO$_2$ at different scan rates ranging from 30–190 mV/s in 0.1 M PBS (pH = 7). Inset: plot of NaNO$_2$ oxidation current w.r.t square root of scan rate. (B) CV responses of AgNS/GCE as a function of NaNO$_2$ concentration in 0.1 M PBS (pH = 7.0) at a scan rate of 50 mV/s. Inset: corresponding calibration plot of current vs. concentration of NaNO$_2$.

$$Ag^0 - NO_2^- \rightarrow \left(Ag^0 - NO_2\right) + e^- \tag{1}$$

$$\left(Ag^0 - NO_2\right) \rightarrow Ag^+ + NO_2 + e^- \tag{2}$$

$$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \tag{3}$$

$$Ag^+ - NO_2^- + e^- \rightarrow \left(Ag^0 - NO_2^-\right) \tag{4}$$

$$NO_2^- + H_2O + e^- \rightarrow HNO_2^- + OH^- \tag{5}$$

To evaluate the role of pH on the catalytic activity of the silver nanospheres, cyclic voltammetric experiments were conducted in the pH range 5–9 in 0.1 M PBS with 3 mM sodium nitrite. As seen in the Figure 2B, maximum current for nitrite oxidation was obtained in a solution of pH 7 and the potential was also least at this pH. Variation of the potential and current in the presence of different protonic concentration implies the involvement of proton in the effective adsorption of the nitrite ions on the catalytic sites as suggested in the earlier studies [39, 40]. In the present study this effective adsorption of the nitrite ions on the catalytic sites is more favored at neutral pH. To get an insight into the underlying basic mechanism behind the electrocatalytic activity of the silver nanospheres towards nitrite oxidation, experiments were performed at different scan rates and concentrations of the nitrite using cyclic voltammetric technique. It was found that the oxidation currents increased with increase in scan rate as shown in Fig 3 A with the potential showing a positive shift. The linear relationship between currents and (scan rate)$^{1/2}$ (Figure 3 inset) with high correlation coefficient of 0.9982, confirms that the oxidation process of nitrite on the silver nanospheres is a diffusion controlled electrochemical process. Figure 3B shows the

electrochemical response under various concentrations of nitrite ranging from 1 to 10 mM. The current increased with the concentration of nitrite, indicating that silver nanospheres exhibited excellent electrocatalytic activity towards nitrite oxidation. Linear variation of the current with nitrite concentration (higher end) suggests the employability of these nanospheres for electrochemical sensing of nitrite even at higher concentrations.

To explore the possibility of using these silver nanospheres for the detection of very small quantities of nitrite, amperometric experiments were conducted under different concentrations of nitrite ranging from 0.1 to 8 μM. At an applied potential of 0.86 V under uniform stirring of 0.1 M PBS (pH 7) successive addition of nitrite was done at regular intervals of 50 seconds and the amperometric response was recorded as shown in the Figure 4 A. The AgNS were highly sensitive even at the least concentration studied and showed linear increase in current with increase in concentration of the nitrite. The amperometric current response shows a linearity with nitrite concentrations ranging from 0.1 to 8 μm with a high correlation coefficient 0.9993 (Figure 4B). The limit of detection and sensitivity were calculated to be 0.031 μM and 580 μA/mM/cm^2 respectively. These values are comparable with different metal nanoparticles prepared using general methods of synthesis and also the biosynthesized silver nanoparticles as tabulated in Table 1. The AgNS synthesized in present study the are prepared using a waste from the pulp industry without any further treatments except for the filtration and dilution.

The catalytic activity of an electrochemical sensing system is affected in the presence of ions or compounds other than the analyte. A good sensor should show little or nil response towards these interfering species to be
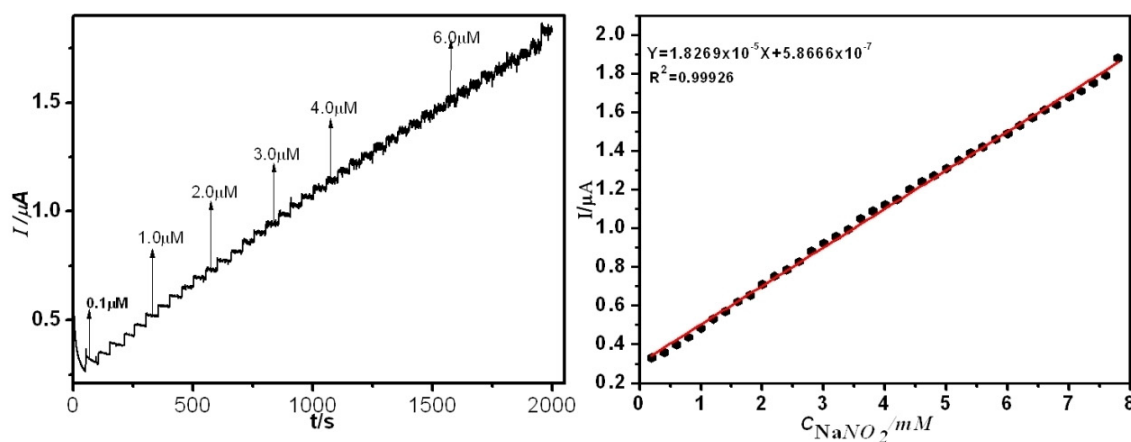
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Fig. 4. (A) The amperometric i-t response of AgNS/GCE with successive addition of $NaNO_2$ in 0.1 M PBS (pH = 7.0) at an applied potential of 0.86 V. (B) Calibration plot of the current response at AgNS/GCE as a function of $NaNO_2$ concentration.

Table 1. Comparison of nitrite sensing performance on different electrode materials.

Electrode material	Ep/ V	Sensitivity (μAmM^{-1} cm^{-2})	Linear range (μM)	LOD (μM)	Analytical method	Reference
GC/Ag-AFS[a]	0.92[#]	0.43	1-16000	0.07	Amperometry	40
AgNPs	1.0*	1642.27	1-6000	0.046	Amperometry	4
Ag-NEEs[b] Modified GCE	0.92[#]	–	10-300	–	Cyclic Voltammetry	32
FeT4MPyP/CuTSPc[c] modified GCE	0.71[#]	–	0.5-7.5	0.14	DPV[f]	41
P-NiTAPc[d]/GCE	0.86[#]	–	2.5-10000	0.90	Cyclic Voltammetry	42
Ag-P(MMA-co-AMPS)[e] modified GCE	0.90[#]	104.6	1-100000	0.2	Amperometry	5
AgPs-IL–CPE[g]	0.87*	–	50-1000	3.0	Squre wave Voltammetry	9
rGO/AgNPs/poly(PyY)[h]	0.86*	13.5	0.1-1000	0.012	Amperometry	37
Ag-RGO nanocomposite	0.60[#]	373.46	10-1000	-	Amperometry	43
GC/GO–Ag nanocomposite	0.92[#]	-	0-12	37	Amperometry	44
AgNS	0.86*	580	0.1-8	0.031	Amperometry	This work

*silver-silver chloride electrode [#] saturated calomel electrode
[a]Amine functionalized silica
[b]Silver nanoelectrode ensembles
[c]Iron(III) tetra-(N-methyl-4-pyridyl)-porphyrin and copper tetrasulfonated phthalocyanine
[d]Polymeric nikel tetraaminothphalocyanine
[e]Methyl methacrylate and 2-acrylamido-2-methylpropane sulfonic acid
[f]Differential pulse voltammetry
[g]Ionic liquid/silver particle-decorated carbon paste electrode
[h]reduced graphene oxide silver nanoparticles polymerization pyronin

practically viable. In order to validate the selectivity of the AgNS towards nitrite sensing, interference study was carried out. Common interfering species such as potassium chloride (KCl), sodium chloride (NaCl), ammonium nitrate (NH_4NO_3), glucose, urea, magnesium nitrate ($Mg(NO_3)_2$), calcium chloride($CaCl_2$), sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), ammonium chloride (NH_4Cl) at 100 times higher concentrations were added at regular intervals separately in between nitrite additions to 0.1 M PBS, pH 7 solution under stirring. The i-t curve

(Figure 5) showed current response only when nitrite was added while remained silent when the interfering ions were added. This study clearly indicates that AgNS are highly selective towards nitrite ions under the experimental conditions studied and hence can be used for electrochemical sensing of nitrite even in the presence of other species in the analyte sample.

The stability of the catalyst was monitored by recording the catalytic activity for 10 cycles every day over a period of 30 days in the pH 7, 0.1 M PBS solution. The
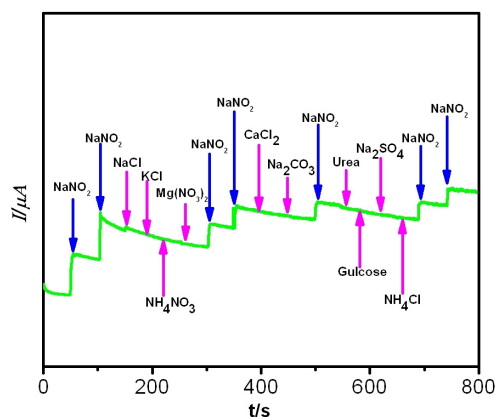
Fig. 5. The selectivity test of AgNS/GCE on addition of 1 μM NaNO$_2$ and 100 μM interfering species namely KCl, NaCl, NH4NO$_3$,Mg(NO$_3$)$_2$, CaCl$_2$, Na$_2$CO$_3$, Na$_2$SO$_4$, NH$_4$Cl, urea and glucose in 0.1 M PBS (pH = 7.0) at an applied potential of 0.86 V.

electrode was stored in water when not in use. The oxidation current and the oxidation potential did not change significantly even after several scans and several days of storage. Figure S3 of the supporting information shows the cyclic voltammetric response of the electrode on the first and the 30th day towards nitrite oxidation in a fresh solution. This unchanged potential and current values revealed that the catalytic surface fouling by the oxidation products was minimum. Reproducibility of the catalytic activity of the AgNS/GCE was tested by carrying out the nitrite oxidation with four different glassy carbon electrodes loaded with same amount of AgNS. The oxidation currents for nitrite at 0.86 V at these four electrodes show a very small change with a RSD of 3.6 % (three repeated experiments for each electrode). These results on stability and reproducibility of the catalyst show that the AgNS/GCE can serve as reliable platform for long term application towards electrochemical nitrite sensing.

The feasibility of employing the sensing system based on silver nanospheres prepared in this work for real sample analysis was also explored by standard-additions method. Tap water was added to pH 7, 0.1 M PBS and the diluted solution was spiked with different known concentrations of nitrite. Satisfactory recoveries (average recovery ranging from 98–106 % with n = 3) of nitrite concentrations were obtained indicating the viability of employing the sensor for real sample analysis as shown in the Table 2.

4. Conclusion

Stable, nanocrystalline, AgNS having *FCC* structure are synthesized using pre-hydrolysed liquor of *Niligiri* wood, a waste from pulp industry as a source of reducing and

Table 2. Recovery data for nitrite determination in tap water on AgNS/GCE.

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD(%) (n = 3)
Tap water	0.0	0.0	-	-
	5.0	5.1	102	2.15
	10.0	10.6	106	2.46
	15.0	14.8	98.66	3.07

stabilizing agent at room temperature. The reaction time is 2–3 hours for the completion of the synthesis and the products are purified by simple washing with water and ethanol. The particles are spherical in shape with an average diameter of 30 nm as revealed by TEM. The AgNS/GCE shows an excellent electrocatalytic activity for the oxidation of nitrite and the corresponding linear range and limit of detection are from 0.1 to 8 μM and 0.031 μM, respectively. The interference study showed no meddling from different species with the determination of nitrite and this exhibits the good selectivity of the sensor. Although the electrochemical activity of these AgNS towards nitrite sensing is comparable with reports in the literature, the potential at which nitrite oxidation occurs is low compared to other systems and the silver nanoparticles prepared by biosynthesis. The sensitivity of the AgNS is high compared with AgNPs reported in literature. The recoveries achieved for the determination of nitrite in tap water indicates the real-world utility of this sensor.

Highlights

1 Green synthesis of AgNS at room temperature using pre-hydrolysed liquor (rich in hemicellulose), a waste from pulp and paper industry that serves as reducing and stabilizing agent.
2 AgNS modified electrodes show a high sensitivity, low detection limit, good reproducibility and long-term stability towards nitrite detection.
3 The proposed sensor was successfully utilized to detect nitrite in tap water.

Acknowledgments

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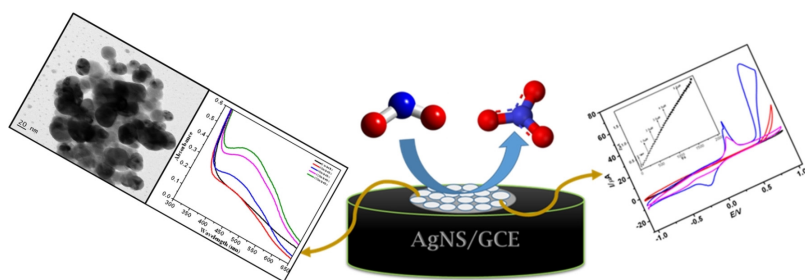
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**Electrochemical detection of
nitrite using glassy carbon
electrode modified with silver
nanospheres (AgNS) obtained by
green synthesis using pre-hydro-
lysed liquor**