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Electrochemical analysis of nitrite contamination in water using SnTe@GO modified glassy carbon electrode

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An electrochemically active tin telluride (SnTe) decorated graphene oxide (GO) (SnTe@GO) nanocomposite has been synthesized through simple experimental method and used the same for surface modification of glassy carbon electrode, thus developed a new efficient SnTe@GO/GCE which in turn has been demonstrated as a sensor for identification and quantification of nitrite species in water samples. Common analytical techniques are employed and established the physiochemical properties of SnTe@GO nanocomposite. The electrocatalytic activity of SnTe@GO/GCE has been examined towards sensing and quantification of nitrite through Cyclic Voltammetry and Differential Pulse Voltammetry techniques. The obtained results revel that SnTe@GO/GCE exhibited high sensitivity with wide linear range such as 9.8-162 μM and detection limit found to be 0.079 μM. In addition, in order to inspect the real time application of SnTe@GO/GCE, it is also employed and determined the concentration of nitrite in drinking water, pond water and well water samples which are collected from Rayapuram, Muttukadu and Guindy during the specific period. The LOD observed for drinking water collected from Rayapuram, Chennai are 1.63 μM, pond water collected from Muttukadu, Kanchipuram 2.5 μM, and the well water collected from Guindy, Chennai are 1.25 μM, and thus proves that the newly designed SnTe@GO/GCE is an excellent sensor for nitrite species even in real water sample analysis.

Keywords: Grpahene oxide, Nitrite, Sensor, Tin Telluride, Voltammetry

Recently, tin chalcogenides have received more interest due to their non-toxicity and layer dependent properties[1-4]. Among the tin chalcogenides, tin telluride is a narrow band gap semiconductor (0.18 eV at 300 K) and exhibits excellent thermoelectric properties[2,5-7]. It has application in a mid infrared photo detector and thermo electric heat converter[8,9]. In addition, nano SnTe crystals used in photovoltaic devices[10], sensor, laser material, thin films polarizer and thermo cooling materials[11]. Recent works on this material are GO-β-SnTe composite for sodium and lithium ion batteries[12], cubic SnTe for sodium and lithium ion batteries[13], tellurium-tin based electrodes for energy storage applications[14]. Based on the reports tin telluride can be a promising material for electrocatalysis related applications. To improve its conductivity and avoid aggregation, and increase the electrocatalytic activity, there is an urge of matrix such as graphene oxide (GO). Due to the large surface to volume to ratio, 2D structure, economical and high conductivity, unique thermal, electronic, optical and mechanical properties it can be used as base matrix for anchoring other sites[15,16]. Therefore, in this study it is decided to decorate SnTe on GO which act as matrix and thus obtained SnTe@GO nanocomposite.

Nitrite (NO_2^-) is available in food industry as a colouring agent and preservative, waste water, and drinking water[17]. It is usually co-exists in ecosystem in biological perspectives and the excess amount of nitrite react with amines to form carcinogenic N-nitrasoamines[18,19]. As per the WHO, the maximum limit of nitrite (NO_2^-) in drinking water is 3 mg/L[20]. In this background, quantitative determination of nitrite is important particularly when the ground water pollution by nitrite is a challenging task. Several analytical tools are already available for determination of nitrite such as, spectrophotometry[21], chemiluminescence[22], capillary electrophoresis[23], chromatography[24] and electrocatalysis[25]. Among the techniques, electrocatalysis holds the advantage of simplicity, high sensitivity and selectivity and low cost[26]. Therefore, in this study, we determined the nitrite using electrochemical analysis such as though fabricating SnTe@GO nanocomposite on to the GCE. To the best of our knowledge, there are no other reports available on electrochemical determination of nitrite using SnTe@GO nanocomposite. In addition, the synthesized SnTe@GO nanocomposite was characterized by XRD, FTIR, SEM, and EDAX techniques. Similarly, the real time application of the present electrode is verified using drinking water, pond water and well water which were collected nearby places.

Materials and Methods

Materials

Powdered graphite (Particle size 48 mm, 99.95% Purity), tellurium tetra chloride ($TeCl_4$), were purchased from Sigma-Aldrich. Tin chloride ($SnCl_2$), polyvinyl propylene, sodium borohydrate ($NaBH_4$), sodium hydroxide (NaOH) and ethanol were obtained from Sisco Research Laboratory (SRL) Pvt. Ltd. About 0.1M of phosphate buffer solution was prepared by mixing 0.27 g of NaH_2PO_4, and 2.14 g of Na_2HPO_4 in 100 mL of DI water.

Synthesis of SnTe

SnTe compound was synthesized by reductive precipitation method. Initially, 0.1 M $SnCl_2$. $2H_2O$, 0.1 M $TeCl_4$ and 0.3 M of PVP were dissolved in 100 mL of double distilled (DD) water. To that solution, 0.2 M $NaBH_4$ was added drop wise under stirring. Then 12 M of NaOH was added to adjust the pH as well as prevent hydrolysis. The resulting precipitate was centrifuged, washed with DD water followed by ethanol and dried at 100°C for 24 h[27].

Synthesis of Graphene oxide

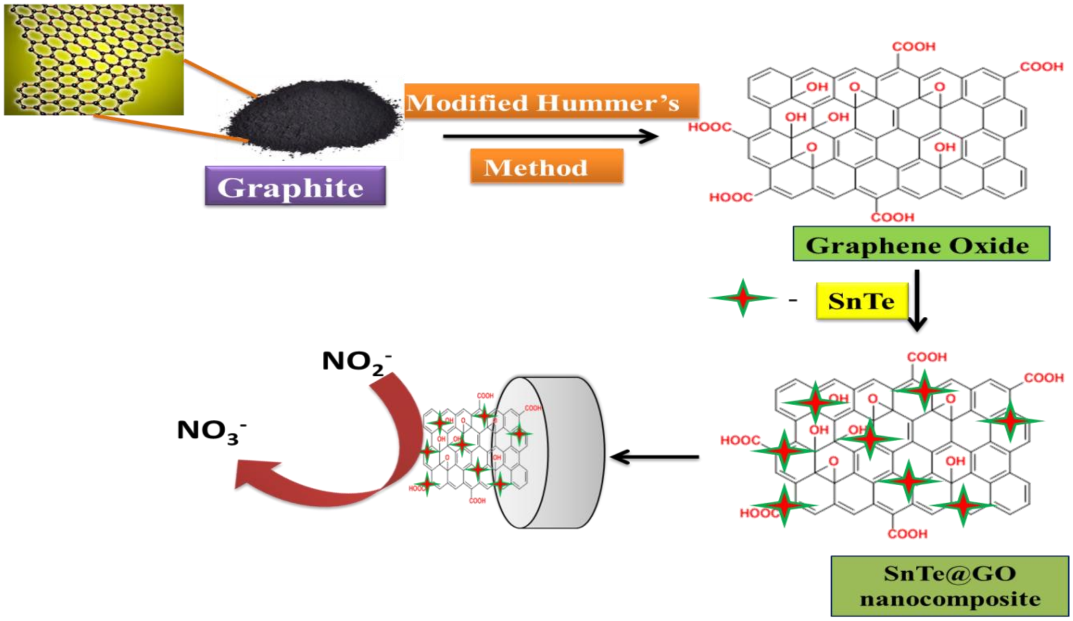
Graphene oxide (GO) was synthesized using the modified Hummers method[28]. Initially, 4 g of graphite and 3.8 g of $NaNO_3$ were mixed in 169 mL of conc. H_2SO_4 in an ice cooled round bottom flask. Then, 22.5 g of $KMnO_4$ was added to it over an hour pinch by pinch. Then ice bath was removed and stirred for 4 days. To that, 500 mL of 5% H_2SO_4 was added to reduce the viscosity and then 25 mL of 30% H_2O_2 was added. After settling the precipitate, the supernatant liquid was removed and re-suspended with a 500 mL of 3% H_2SO_4 and 0.5% H_2O_2 for another two days. Then the precipitate was washed several times with DD water to adjust pH to 7 and then dried at 70°C for 24 h.

Preparation of SnTe@GO nanocomposite

To begin with, in a 100 mL RB flask 0.050 g of GO was taken and dispersed in 40 mL of DD water through sonication for 45 min. To that, 0.1 g of SnTe nanoparticles was added and the resulting suspension was continuously stirred for 3 h at 30°C. The resulting product was washed with water and ethanol. The product was dried at 80°C for 12 h, and thus obtained SnTe@GO nanocomposite (Scheme 1)[29].

Real sample preparation

Triplet samples of drinking water, pond water and well water were collected from three different places, such as Rayapuram (Chennai district), Muttukadu (Kanchipuram) and Guindy (Chennai), respectively. The collected samples were filtrated to remove the suspended solid particles and organic substances and used as stock solutions. From the stock solutions, 20 mL



Scheme 1 — Synthesis of SnTe@GO nanocomposite and electrode mechanism of respective water sample was pipetted out and added to volumetric flask and concentration of nitrite were determined through DPV technique.

Fabrication of SnTe@GO/GC Electrode

Prior to fabrication, glassy carbon electrode (GCE) was cleaned with three different pore size of alumina powder (1.0, 0.5 and 0.05 µm). After that, the GCE was ultrasonically cleaned with water and ethanol. Then, GCE was rinsed in DD water and dried at room temperature. After that 10 mg of the SnTe@GO nanocomposite was dispersed in water and 5 µL is pipetted out and coated on the bare GCE and dried at ambient temperature. For comparison, SnTe/GCE, GO/GCE were also prepared in same way.

Materials characterization

The synthesized SnTe, GO and SnTe@GO nanocomposites were characterized through X-Ray diffraction method and the spectrum was recorded on D8 advanced (bruker) with Cu Kα radiation in the 2θ range 10-80˚. The functional group identification was done through FTIR analysis and the spectrum was recorded on Bruker Tensor instrument. The surface morphology and elemental composition of the synthesized materials were characterized using FE-SEM analysis with EDX (FEI-Quanta FEG 200-High resolution scanning electronic microscope).

Electrochemical measurements

The analyses of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were taken on CHI1130a electrochemical work station with three electrode system. The GCE acted as working electrode (surface area of 0.03 cm^2), Ag/AgCl electrode acted as the reference electrode and platinum wire was used as the counter electrode. PBS (0.1 M) was used as the supporting electrolyte.

Results and Discussion

FE-SEM and EDAX analyses

The morphology of the SnTe@GO composite, GO and SnTe were studied with FE-SEM (Fig. 1 A-C). The GO morphology showed a sheet like structure (Fig. 1A). Fig. 1B shows tiny sphere are arranged into sponge like structure. Fig. 1C demonstrates the general view of the SnTe@GO composite. It shows

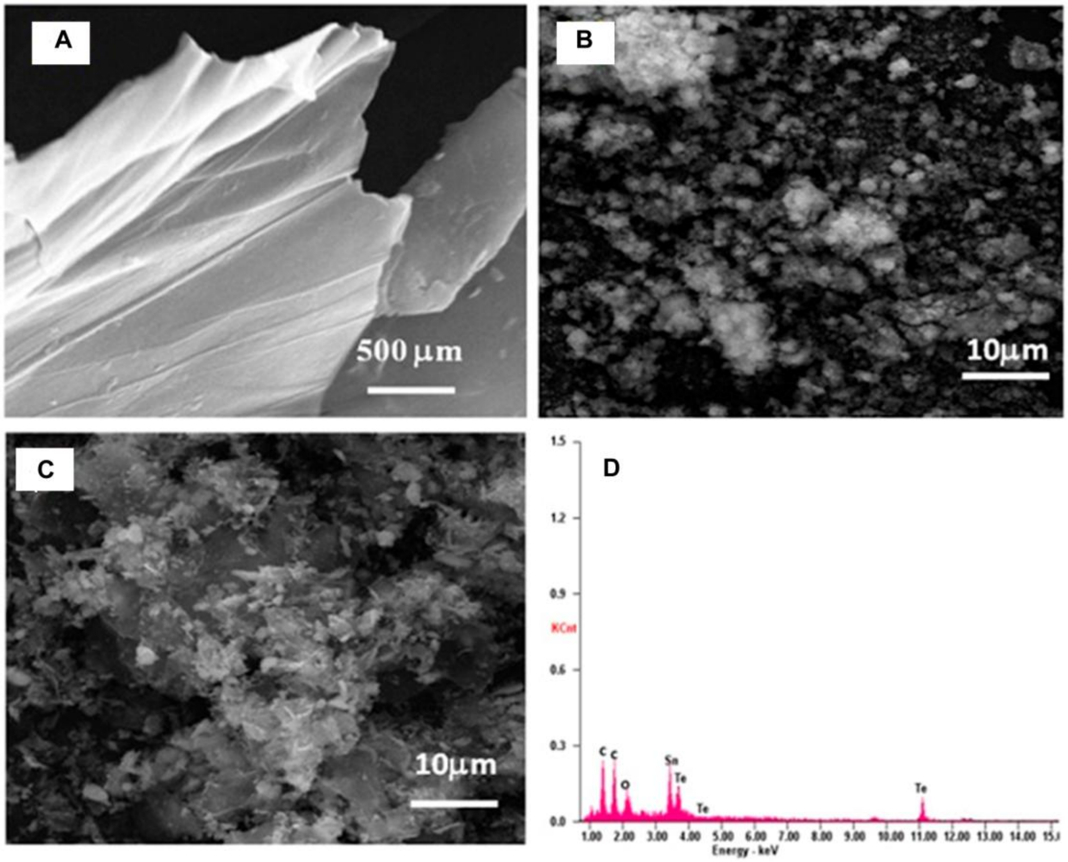


Fig. 1— FE-SEM image of (a) GO, (b) SnTe, (c) SnTe@GO, and (d) EDAX of SnTe@GO nanocomposite

the tiny sphere embedded GO sheets. Fig. 1D shows the EDAX spectrum of the composite. It confirms C, O, Sn and Te elements which constituted to the SnTe@GO composite. All these results confirm the formation of SnTe@GO nanocomposite.

XRD analysis

The powdered XRD was used to determine the phase and crystal structure of the prepared materials. Fig. 2A(i) display the diffraction pattern of layered shape of GO. It shows a peak at 2θ = 11.13˚ due to the (002) of GO. Fig. 2A(ii) shows peaks due to SnTe at 2θ = 28.17˚, 40.34˚, 49.9˚, 58.31˚ and 65.94˚ belongs to the phases of (021), (222), (223), (044) and (245), respectively. All these peaks confirm formation of SnTe[29]. Fig. 2A(iii) shows the XRD pattern of SnTe@GO nanocomposite in which the strong peak observed at 2θ value of 27.74˚ and 42.6˚ corresponding to SnTe and the peak at 12.17 corresponds to the layered GO. The XRD spectrum confirms the formation of SnTe@GO nanocomposite.

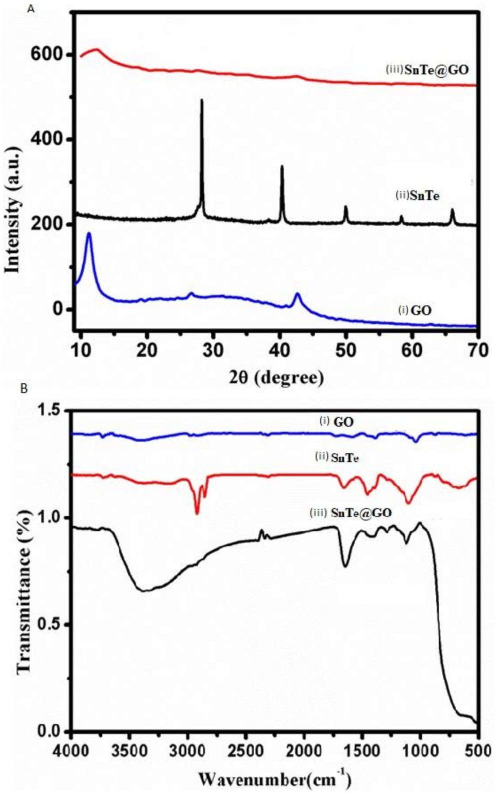


Fig. 2— (A) XRD pattern; and (B) FT-IR spectra of GO, SnTe and SnTe@GO nanocomposite

FTIR analysis

In the FTIR spectrum [Fig. 2B(i)] of GO[30] showed an intense and broad O-H stretching vibration band at 3375 cm^{-1}, carbonyl stretching band occurred at 1651 cm^{-1}, O-H deformation vibration band at 1504 cm^{-1} and C-O stretching vibration at 1120 cm^{-1}. The FTIR spectrum [Fig. 2B(ii)] shows peaks below 300 cm^{-1} due to stretching of the -CH$_2$ group of adsorbed organics on the surface of the SnTe. The peaks between 1300 and 1450 cm^{-1} are due to –CH$_2$ bending modes. The peak around 520 cm^{-1} is assigned to SnTe vibration. The FTIR spectrum of the SnTe@GO composite showed all peaks corresponding to GO and SnTe [Fig. 2B(iii)] and but they were weak. All these results confirm the formation of nanocomposite.

Electrochemical characterization

The electroactive surface area of the GCE was studied using [Fe(CN)$_6$]$^{3-/4-}$ redox probe by CV. The CV results recorded for bare GCE and SnTe@GO/GCE in the presence of 1.0 mm of [Fe(CN)$_6$]$^{3-/4-}$ and 0.1 M of KCl at 50 mV/s

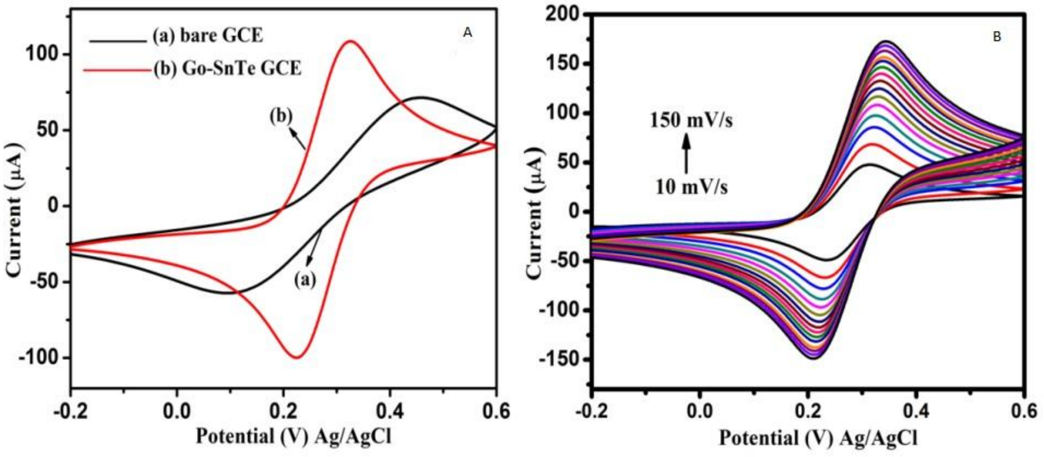


Fig. 3 — CVs of (A) different modified electrodes and (B) effect of scan rate in 0.1 M KCl/ 0.1 M[Fe(CN)$_6$]$^{3-/4-}$ at SnTe@GO/GCE

(Fig. 3A). The observed potential difference (ΔEp) for bare GCE is 363 mV which is higher than the SnTe@GO/GCE (101 mV). The smaller ΔEp and improved redox peak current on SnTe@GO/GCE indicates an excellent electron transfer kinetics and large electroactive surface area. The effective surface area of the SnTe@GO/GCE was calculated using Randles-Sevick equation[31] such as

$$Ip = (2.69 \text{ X } 10^5)\, n^{3/2} D^{1/2} C\, A\, V^{1/2} \qquad (1)$$

where A represents the microscopic area of the working electrode, n the number of the electrons (n =1) D s diffusion co-efficient, C the concentration of the $[Fe(CN)_6]^{3-/4-}$ (1 mM) and ν the scan rate (V/s).

From the plot of current *vs*. square root of the scan rate ($\nu^{1/2}$) (Fig. 3B), the surface area of the bare GCE and SnTe@GO/GCE were calculated and they were equal to 0.03 and 0.8528 cm^2, respectively.

Electrochemical detection of nitrite

To evaluate the electrocatalytic activity of the synthesized materials, the electrochemical oxidation of nitrite was carried out as model reactions. Cyclic voltammograms (CVs) were recorded for bare GCE, SnTe/GCE, GO/GCE and SnTe@GO/GCE in the presence of 0.1 mM of nitrite and shown in Fig. 4A(a-d), respectively. There is no peak potential observed for bare GCE whereas the SnTe/GCE, GO/GCE showed high over potential for oxidation of nitrite (Fig. 4B). But SnTe@GO/GCE showed a higher electro activity than bare GCE which are almost 2.35 times higher. The observed oxidation potentials of nitrite at different electrodes were presented in Table 1.

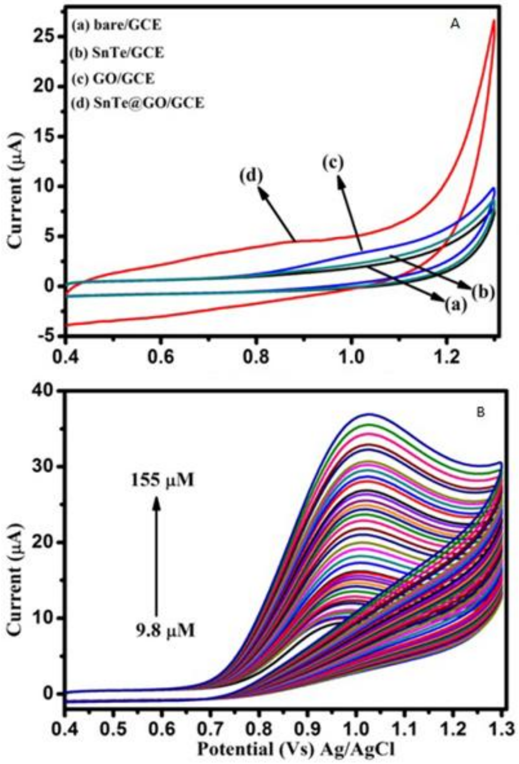


Fig. 4 — (A) CVs of (a) bare GCE, (b) SnTe/GCE, (c) GO/GCE and (d) SnTe@GO/GCE in 0.1 M PBS containing 1.0 mM nitrite at a scan rate of 50 mVs^{-1}; and (B) various concentration of nitrite

A possible mechanism for the electro-catalytic oxidation of nitrite at the SnTe@GO/GCE is given below and it involves two electron transfer mechanism[32].

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

Influence of Scan rate and nitrite oxidation

Fig. 5A shows the effect of scan rate from 10 to 100 mV s^{-1} for electro-catalytic oxidation of nitrite on

Table 1 — Peak potentials and peak currents for nitrite oxidation at different electrodes

Electrode	Epa (V)	Ipa (μA)
bare GCE(Control)	1.04	1.84
SnTe	1.05	2.803
GO	0.99	3.062
SnTe@GO/GCE	0.875	4.35

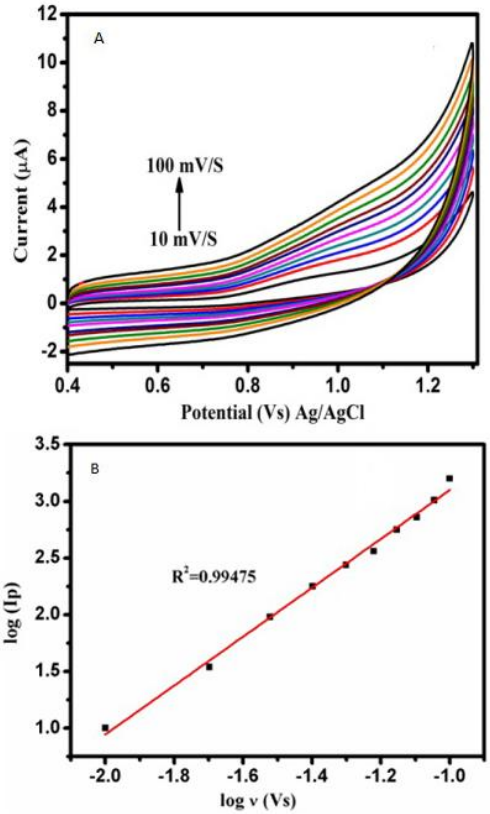


Fig. 5 — (A) CVs of SnTe@GO/GCE in 0.1 M PBS (pH 7.2) containing 1.0 mM nitrite at various scan rates 10-100 mV s^{-1}, and (B) the calibration plot of log Ip *vs*. log scan rate

SnTe@GO/GCE in 0.1 M of PBS (pH 7.2) containing 1.0 mM nitrite. On increasing the scan rates, the peak currents were also increased linearly and shifted to more positive region. Fig. 5B shows the linear relationship between the log Ip *vs*. log scan rate suggesting the diffusion controlled electro-oxidation process[33].

Determination of nitrite through DPV

Differential pulse voltammetry (DPV) is the highly sensitive, selective technique. The electro-chemical response of nitrite oxidation for various concentrations at SnTe@GO/GCE is shown in Fig. 6A. The oxidation of nitrite occurs at 0.78 V in which the peak current is significantly increased on increasing the concentration from 9.8 to 168 μM. Thus confirms the excellent electrocatalytic activity of the present SnTe@GO/GCE. The linear response is shown in Fig. 6B. The obtained results of SnTe@GO/GCE was compared with literature and given in Table 2[34-38]. This confirms low limit of detection (LOD), wide linear range and higher sensitivity of the SnTe@GO/GCE. These results are proves the excellent electrocatalytic activity of the SnTe@GO/GCE.

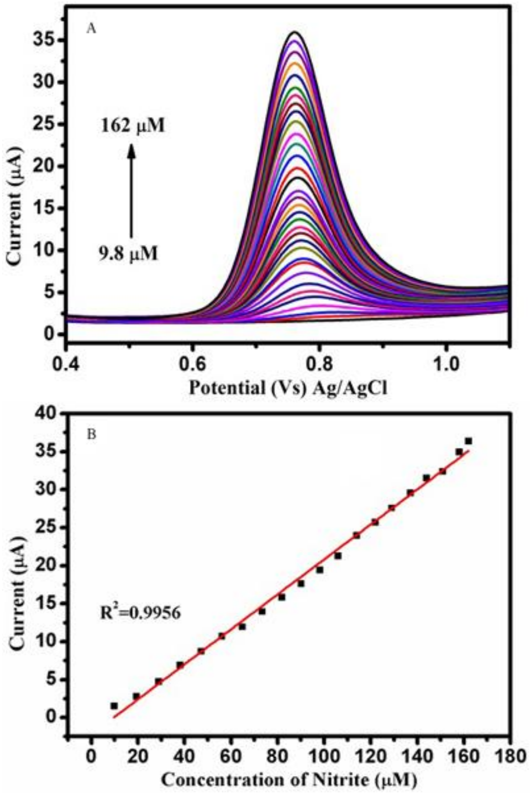


Fig. 6 — DPV curves obtained for (A) different concentration of nitrite in 0.1 M PBS; and (B) the calibration plot of peak current *vs*. nitrite concentrations

Detection of nitrite in real samples

The real time applicability of the present sensor was verified by applying SnTe@GO/GCE for determination of nitrite in various forms of water using standard addition method (Table 3). The results showed the recovery of the sample ranged from 98, 104 and 95%. The results confirm the efficiency of the proposed sensor towards the determination of the nitrite in water samples with good recovery rate.

Anti-interference study

To establish the anti-interference property of the SnTe@GO/GCE, the oxidation of nitrite was examined in the presence of F^-, Cl^-, Br^-, CO_3^{2-}, HCO_3^-, Mg^{2+}, Ca^{2+}, Cd^{2+}, Cu^{2+}, NH_4^+ at 100 fold concentration of NO_2^-. No interference was observed. These results prove the suitability of the present sensor for practical applications.

Stability, reproducibility and repeatability

The SnTe@GO/GCE electrode was stored for ten days in 0.1 M PBS and 100 μL of 0.01 mM Para at room temperature to check the long term stability.

Table 3 — Analysis of nitrite in different types of water samples at SnTe@GO/GCE

Sample	Added (μM)	Found (μM)	RSD (n=3)
Drinking water	5	4.9	2.3
Pond water	7	7.3	1.01
Well water	4	3.8	0.9

Table 2 — Comparison of analytical parameters of electrocatalytic oxidation of nitrite at different electrodes.

Electrodes	Technique	LOD (μM)	LDR (μM)	Ref.
Nf/Fe(bpy)$_3^{2+}$ modified GCE	CV	30	200-20000	34
(p-NiTAPC) modified GCE	DPA	0.1	0.5-8000	35
Au/Fe(III) nanoparticle modified electrode	DPA	0.2	0.3-150	36
MnO_2-CP EPOXY composite electrode	LSV	0.6	20-200	37
FeT$_4$M PYP/CuTSPC modified electrode	DPV	0.14	0.5-7.5	38
SnTe@GO/GCE	DPV	0.079	9.8-162	This Work

[Nf/Fe(bpy)$_3^{2+}$ modified GCE: Immobilized iron (2,2'-bipyridyl) on Nafion; (p-NiTAPC) modified GCE: Polymeric nickel tetraaminothphalocyanine; MnO_2-CP EPOXY composite electrode: Manganese dioxide graphite composite; FeT$_4$M PYP/CuTSPC modified electrode: Iron(III) tetra-(N-methyl-4-pyridyl)-porphyrin and coppertetrasulfonatedphthalocyanine; CV: Cyclic voltammetry; DPV:Differential pulsevoltammetry; LSV: Linear sweep voltammetry; DPA: Differential pulse amperometry]

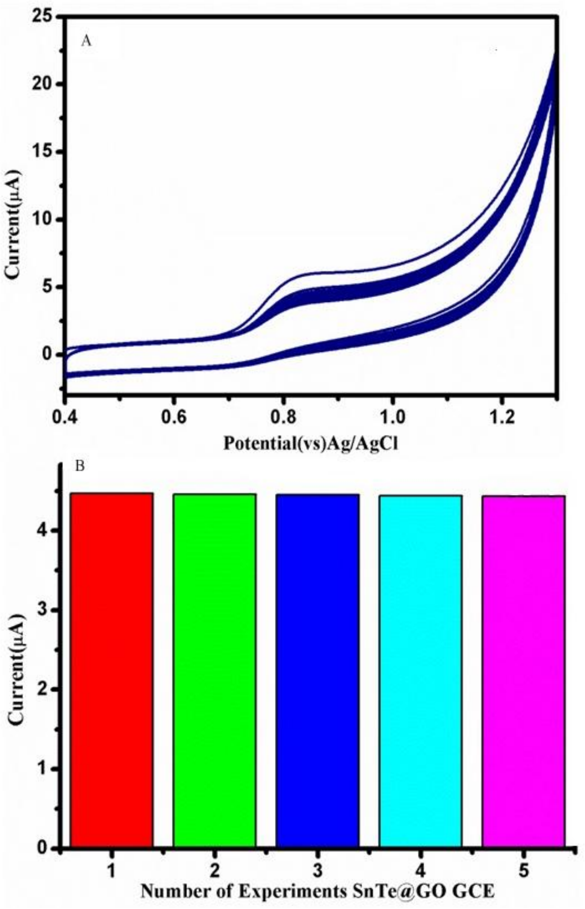


Fig. 7 — DPV curves of (A) Stability of nitrite in 0.1 M PBS and (B) Reproducibility of SnTe@GO/GC Electrode

There is no change in density was observed, thus proves the electrode stability (Fig. 7A). Similarly, the reproducibility of the SnTe@GO/GCE was studied by repeating the same experiments for four times (Fig. 7B), the observed results showed 1.7% RSD proving the good reproducibility. Thus concludes that the SnTe@GO/GCE electrode can be used for practical applications.

Conclusions

The SnTe@GO nanocomposite was synthesized by facile method and characterized the same through XRD, SEM, and EDAX and FTIR techniques. The formation of nanocomposite was strongly confirmed using XRD technique. Then the surface of GCE is modified with this composite, and thus obtained efficient SnTe@GO/GCE electrochemical sensor. The electrochemical efficiency of the synthesized electrode was evaluated through sensing and determination of nitrite. On comparing the CV results of control electrodes such as bare GCE, SnTe/GCE and GO/GCE, the SnTe@GO/GCE showed significant increase in oxidation current and peak potential also shifted towards negative. Similarly, the DPV results showed significant increase with increase in the concentration from 9.8 to 162 μM with LOD of 0.079 μM. The SnTe@GO/GCE showed excellent sensitivity, and wide linear range with lower detection limit. More importantly, it is noteworthy to highlight here that this newly developed electrode was employed and examined for sensing and determination of nitrite concentration in drinking water, pond water, and well water samples and that the electrode showed good recovery rate such as 98, 104, and 95%, respectively. Therefore, the results of this study provide a way to utilize the tin telluride for real sample analysis and quantification of nitrite in various water samples.

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Conflict of interest

The authors declare no conflict of interests in this study.

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