Research Article

Polynuclear Nickel Hexacyanoferrate/Graphitized Mesoporous Carbon Hybrid Chemically Modified Electrode for Selective Hydrazine Detection

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A hybrid polynuclear nickel hexacyanoferrate (NiHCFe)/graphitized mesoporous carbon- (GMC-) modified glassy carbon electrode (GCE/NiHCFe@GMC) has been prepared by a sequential method using electrodeposited Ni on a GMC-modified glassy carbon electrode (GCE/Ni@GMC) as a template and [Fe(CN)₆]³⁻ as an in-situ chemical precipitant, without any additional interlinking agent. Physicochemical and electrochemical characterizations reveal the presence of NiHCFe units within the porous sites of the GMC. The GCE/NiHCFe@GMC electrode showed highly stable and well-defined redox behaviors with surface-confined electron-transfer mechanism in a pH 7 phosphate buffer solution. The GCE/NiHCFe@GMC showed about 20 times enhancement in hydrazine oxidation peak current along with 500 mV reduction in overpotential over the corresponding unmodified GCE/GMC. Hydrazine calibration plots by CV and amperometric i-t methods were linear up to 1 mM and 220 μM with current sensitivity values of 15.86 μA/mM and 7.37 nA/μM, respectively. Calculated detection limit by the amperometric i-t method was 23.2 nM. The hybrid GCE/NiHCFe@GMC exhibits remarkable tolerance to important industrial and biological interferents. Finally determination of hydrazine in cigarette smoke sample was successfully demonstrated.

1. Introduction

Hydrazine is a toxic and carcinogenetic chemical used for several industrial, environmental, and aerospace applications (as a fuel). A burning cigarette produces hundreds of gaseous and particulate compounds including hydrazine (31.4 ng/ cigarette) in the smoke formed by pyrolysis or combustion of tobacco [1, 2]. Sufficient information is available on the carcinogenic effects of hydrazine and its derivatives in experimental animals [1, 2]. Hydrazine is used in agricultural, chemical blowing agents, pharmaceutical intermediates, photography chemicals, boiler water treatment for corrosion protection, and as a fuel for rockets and space craft [3–6]. Hydrazine itself or its sulphate salt has been used in the treatment of tuberculosis, sickle cell anemia, and some of the chronic illnesses [7, 8]. Thus, sensitive and selective detection of hydrazine in real samples is of significant research interest in analytical chemistry. For hydrazine real-sample analysis, various spectroscopic and chromatographic methods especially derivatization approach, where hydrazine reacted with pentafluorobenzaldehyde to form corresponding decafluorobenzaldehye azine [9], have been reported. The conventional assays require tedious sample preparation and time-consuming instrumental procedures [9, 10]. Meanwhile, some electroanalytical techniques were also adopted for the quantitative determination of hydrazine real-sample analyses. For example, copper-palladium alloy nanoparticle plated electrode and barrel plated rhodium nail electrode for the determination of hydrazine in tobacco and water samples, respectively [11, 12]. Note that the electroanalytical techniques have several advantages over the conventional spectroscopic methods which include portability of the working instrument, less sample preparation duration, direct measurements and extendibility to disposable type screen-
printed electrodes systems and so forth. In this work, we are reporting a polynuclear nickel hexacyanoferrate (NiHCFe)/graphitized mesoporous carbon (GMC) modified glassy carbon electrode (designated as GCE/NiHCFe@GMC, GCE: glassy carbon electrode) prepared by cathodically deposited Ni on GMC-modified GCE as a template (GCE/Ni@GMC) and [Fe(CN)₆]³⁻ as a precipitant for stable and physiological solution (pH 7 sodium phosphate buffer solution, PBS) operable electro-catalytic oxidation of hydrazine.

As an important class of fairly well-defined zeolite-like polynuclear inorganic mixed-valence compounds, transition metal hexacyanoferrate (MHCFe, M = Fe, Ni, Co, and Ru) also referred as Prussian blue analogues have received wide research interest because of their interesting electrochemical properties [13–17]. Among the Prussian blue analogues, polynuclear nickel hexacyanoferrate ([NiII]−NC−FeIII−CN−NiIII−/NiII− net work; NiHCFe) has gained special attention due to its well-defined single reversible redox peak in the presence of alkali metal ion solution [16, 18–20]. Few papers reported ex situ deposited NiHCFe/CNT hybrid units, where a mixture containing Ni²⁺ and Fe(CN)₆³⁻ was first converted to NiHCFe complex particles, and then they were allowed to assemble/adsorb on the CNT [21–26]. Recently our group found out a new in situ route for stable immobilization of NiHCFe on a functionalized multiwalled carbon nanotube modified GCE (GCE/NiHCFe@f-MWCNT, f: functionalized) and for selective hydrazine electrocatalytic oxidation [27]. However, in consideration with cost, purification, functionalization, and complication with the metal ion impurities, the CNTs will not be a good choice as a matrix for hybrid electrode formation. Alternately, in this work, we are introducing a low-cost and metal ion impurity-free carbon material, graphitized mesoporous carbon (GMC) as a matrix to immobilize NiHCFe and for efficient electrocatalytic oxidation of the hydrazine in a physiological solution. Finally, a cigarette smoke real-sample analysis was demonstrated with the above electrode.

2. Experimental Section

2.1. Reagents and Materials. Graphitized mesoporous carbon (>99% purity) was purchased from Aldrich, nickel chloride hexahydrate (NiCl₂·6H₂O) was obtained from Central drug house (P) Ltd, potassium ferricyanide from Merck, and hydrazine sulphate extra pure from Sisco’s Research Laboratories, India. Other chemicals were of analytical grade and used as received without further purification. Aqueous solutions were prepared using deionized and alkaline KMnO₄ distilled water (designated as DD water). Unless otherwise stated, a pH 7 phosphate buffer solution (PBS) of ionic strength 0.1 M was used as a supporting electrolyte in this study.

2.2. Apparatus. Voltammetric measurements were carried out using CHI model 660C electrochemical work station, USA with 10 mL working volume. The three-electrode system consisted of glassy carbon electrode (GCE) of 0.0707 cm² geometrical surface area and its chemically modified form (CME) as a working electrode, Ag/AgCl with 3 M KCl as a reference electrode, and platinum wire as a counter electrode. Bioanalytical system (BAS, USA) polishing kit was used to polish the GCE surface. The surface of the GCE was cleaned first mechanically by polishing with 500 micron alumina powder, washing with DD water, and sonicating for 5 min. The electrochemical pretreatment procedure consisted of potential cycling of the above electrode in a potential window from 0 to 0.9 V versus Ag/AgCl continuously for 10 cycles (n = 10) at a potential scan rate (v) of 50 mV s⁻¹ in a pH 7 PBS.

2.3. Procedures. A GMC stock solution was first prepared as a suspension by mixing 1 mg of the GMC in 500 μL ethanol. Prior to the surface coating, the stock solution was sonicated for 3–5 min, and 5 μL of the suspension was drop-coated on the pretreated GCE (designated as GCE/GMC). It was allowed for ∼3 minutes in air for complete drying. The modified electrode was electrochemically pretreated for twenty continuous cycles (n = 20). There was no sign of any faradaic electron-transfer behavior with the GCE/GMC. All experiments were performed with normal dissolved oxygen (DO) that closely resembles the physiological system.

Scheme 1 illustrates preparation of the GCE/NiHCFe@GMC by a template-assisted procedure in two steps. Step 1 consists of preparation of GCE/Ni@GMC, where Ni²⁺ was cathodically deposited on the GCE/GMC from a solution containing 6 mM NiCl₂ in 0.1 M pH 7 PBS at an applied potential (E_app) of −0.9 V versus Ag/AgCl for 180 s (optimal). The GCE/Ni@GMC electrode was used as a template in Step 2 for the GCE/NiHCFe@GMC preparation. In this procedure, the template was subjected to potential cycling treatment in presence of 1 mM K₂[Fe(CN)₆] in a potential window of 0 to 0.9 V versus Ag/AgCl with a scan rate of 50 mV/s (n = 20). This procedure allows the in situ formation of NiHCFe units, where the Ni active sites are formed, within the GMC (Scheme 1(c)). The modified electrode is referred as GCE/NiHCFe@GMC. After preparation, the electrode was washed with DD water and conditioned by CV potential cycling again in the potential range of 0 V to 0.9 V for 20 times in a blank pH 7 PBS at v = 50 mV s⁻¹. Control NiHCFe-modified GCE was also prepared (GCE/NiHCFe) in a similar way as mentioned above without any GMC coating on the GCE.

For the case of scanning electron microscopy (SEM) characterization (HITACHI SU 6600, Japan), NiHCFe@GMC particles scratched out from the GCE/NiHCFe@GMC system were taken for the analyses.

2.4. Real-Sample Analysis. A branded cigarette pack was purchased from local shop and used without any pre-treatment. The cigarette smoke was collected in 0.1 M pH 7 PBS (N₂ purged) using a dreschel’s bottle. In that procedure, burning cigarette (four numbers successively) was first placed on one end of the glass tube of the dreschel’s bottle which is immersed in 150 mL pH 7 PBS. The other glass tube was connected to a suction pump, which was used to suck the smoke into the bottle. The cigarette smoke gases were
bubbled through the 150 mL PBS. The smoke gas-dissolved solution was taken as a test sample for electro-analysis. 100 μL of the real-sample aliquots was spiked into 10 mL of the working cell for the real-sample analysis. For the hydrazine quantification assay, standard addition method was adopted.

3. Results and Discussions

3.1. SEM Characterization of the NiHCFe@GMC. Figure 1 shows typical SEM images of GMC (a) and NiHCFe@GMC (b) and (c). The GMC shows agglomerated clusters of several individual particles of size about 50 nm. After the NiHCFe active site modification on the GMC, an average particle size of 118 nm was noticed, and this size is 2.3 times higher than the respective unmodified GMC. Energy dispersive analysis (EDX) of the NiHCFe@GMC shows presence of the following metals with its atomic % percentage values of C (89.26), N (0.89), O (9.39), Na (0.40), Cl (0.17), Fe (0.18), and Ni (0.70) (figure not enclosed). It is surprising that there is no metal intercalation reactions with the stoichiometric form more stronger than the non-stoichiometric form [14]. As a result, the redox potentials of the NaNiII[FeII(CN)6] appeared at Eo′ ∼ 400 mV as an intense peak and NaNi1.5[FeII(CN)6] at Eo′ ∼ 500 mV as a less intense peak [14]. But in the present case with the GCE/NiHCFe@GMC, a reverse in the trend was noticed, where the most intense redox peak appeared at less positive potential (Eo′ ∼ 335 mV), and less intense peak was noticed at Eo′ ∼ 405 mV versus Ag/AgCl in pH 7 PBS. In other words, the nonstoichiometric compound’s redox reaction (1) showed more intense peak current than that of the stoichiometric reaction (2) in this work. It is expected that the NiHCFe-immobilized GMC has specific structure, which may markedly differ from the naked NiHCFe units as reported in the literature [14]. Possibly, as shown in the Scheme 1(c), NiHCFe units might be encapsulated within the porous structure of the GMC and, hence, some difficulty for the alkali metal intercalation reactions. This observation qualitatively resembles with the previous GCE/NiHCFe@f-MWCNT system [27], where the NiHCFe units were immobilized inside the f-MWCNT. Twenty continuous CV responses of GCE/NiHCFe@GMC at a sweep rate of 50 mV/s in pH 7 PBS resulted in a relative standard deviation (RSD) value for the anodic peak current, iap, and peak potential, Eap, of 0.37 and 0.28%, respectively. These low values denote appreciable stability of the modified electrode in a neutral pH unlike the conventional NiHCFe film with poor stability [23, 24, 27].
The optimal preparation method adopted for the GMC/NiHCFe@GMC case was extended to prepare GMC unmodified electrode, the GCE/NiHCFe as in Figure 2(B). Interestingly absence of any NiHCFe film formation on the GCE was noticed. Instability of the naked NiHCFe in neutral pH is the reason for the absence of the NiHCFe film on the GCE. These observations clearly indicate the significance of the GMC as a matrix for the NiHCFe immobilization and for stable physiological solution operation.

From the SEM/EDX measurements, atomic ratio calculated for the Ni/Fe is 3.8, which is significantly higher over the ratio of 1 and 1.5 proposed earlier in the above equations. Presumably there will be some unreacted Ni as nickel oxide inside the GMC, which might be responsible for the higher ratio. Note that the nickel oxide (NiO₂, x = 2) is reported not to be involved in the NiHCFe formation [27].

Effect of scan rate on the redox behavior of the GCE/NiHCFe@GMC was further investigated as in Figure 3(a). A systematic increase in the redox peak currents was noticed upon increase of the voltammetric scan rate (ν). The ratio of cathodic-to-anodic peak currents (iₚc/iₚa) at various scan rates is almost unity, and double logarithmic plots of iₚa and iₚc versus scan rate for A1/C1 redox peak resulted in a slope value (∂log(iₚ)/∂log(ν)) of 0.904 (Figure 3(b)). This number is closer to the ideal value of 1 for a surface-confined electron-transfer mechanism for a redox system [20].

Effect of solution pH on the redox behavior of the GCE/NiHCFe@GMC material was investigated as displayed in Figure 3(c). The peak potential values were independent of the solution pH over the range of 3–10 (Figure 3(d)), suggesting absence of any proton-coupled electron-transfer reaction with the hybrid matrix. This pH-independent observation resembles with the GCE/NiHCFe@f-MWCNT system [27]. This experiment also evidence the good stability of the GCE/NiHCFe@GMC in the pH 3–10 without any fouling characteristic unlike the case of the physically adsorbed NiHCFe on graphite with marked dissolution of mediator at very high basic and acidic pHs [28].

Since alkali metal insertions play a key role in the redox reaction and for charge neutralization of the NiHCFe [29], effect of different alkali metal ions on the electrochemical behaviors of the GCE/NiHCFe@GMC was investigated by using CV. For the measurements, known amount of alkali metal ion was added with pH 7 PBS, and CV was run. Note that for unknown reasons the alkali metal ion-constituted in the PBS, was never utilized by the NiHCFe-modified electrode for the charge neutralization [27]. Figure 4(a) is the typical CV responses of GCE/NiHCFe@GMC in presence of added 0.1 M of Na⁺, Li⁺, K⁺, NH₄⁺, and Ba²⁺ in a pH 7 PBS. The low ionic radii alkali metals, Li⁺ and Na⁺ did not alter the peak potential values; however, the peak current of the electrode with Li⁺ decreased to 30% when it was
compared with the presence of Na⁺. On the other hand, the high ionic radii alkali metals such as K⁺, NH₄⁺, and Ba²⁺ alter both the peak current and peak potential considerably as in Figure 4(a). In our previous study with GCE/NiHCFe@f-MWCNT, we have noticed similar kind of observations for both low and high ionic radii alkali metals except with the minor variation in the peak current values between Li⁺ and Na⁺ ions [27]. Meanwhile, the naked NiHCFe system was reported to be sensitive to all the alkali metals and, thus, resulted in marked alteration in the peak current and potential values [30]. Overall reasons for the alteration in the redox features are due to (i) ionic size of the alkali metal, (ii) ionic size of the solvated layer, (iii) apparent diffusion coefficient (Dapp) of the alkali metal within the film, and (iv) channel size of the NiHCFe cubic crystal. The nanocubic structure of NiHCFe can allow low ionic radii alkali metals (Li⁺ and Na⁺) to enter freely into the nanochannel, intercalate, and exhibit coupled chemical electron-transfer reactions. The decrease in the peak current response without altering the Eₚₕ in presence of Li⁺ (Figure 4(a)) may be due to its Dapp and to the huge size of the solvated layer Li⁺ ion [27]. There will be some difficulty in entering the porous channels of NiHCFe@GMC by the high ionic radii metals such as K⁺, NH₄⁺, and Ba²⁺, which may result in marked alteration in the peak current and peak potential values of the NiHCFe (Figure 4(a)). Exact detail of the structure and the mechanism in unknown for us now.

In order to get more detailed information about Na⁺ and K⁺ ion-coupled chemical electron-transfer properties, we have investigated the effect of the alkali metal concentration on the redox behaviors of the GCE/NiHCFe@GMC as in Figure 4(d). For the case of Na⁺ ion, specific alteration in the cathodic peak potential (slope ~52 mV/decade; Nernstian behavior with equal amount of Na⁺/e⁻ coupled reaction) and unaltered anodic peak potential behaviors were noticed unlike the totally independent redox behavior with the GCE/NiHCFe@f-MWCNT case [27]. Encapsulation of fraction of Na⁺ ions within the carbon nanotube structure was the reason for the unaltered redox behaviors [27]. Absence of such trapped alkali metal within the GMC matrix might be the reason for the marked alteration in the redox feature of the NiHCFe@GMC unit. In general, anodic and cathodic peaks of NiHCFe can be referred as exertion and insertion of the alkali metal ions, respectively, on the NiHCFe film [27]. For the Na⁺ case, there might be some difficulty in the insertion of the Na⁺ into the porous structure of the hybrid unit, while the exertion could be relatively faster. As proposed in the earlier section, the NiHCFe sites might be formed within the nanopores of the GMC, which could be least accessible by the Na⁺ ion in this work. Next, the effect of KCl concentration on the GCE/Ni-NCFe@GMC redox response was also examined by CV as in Figure 4(c). Plot of Eₚₐ or Eₚₑ versus log[KCl] was given in Figure 4(d). Calculated slope (∂Eₚₐ/∂ log[KCl]) and (∂Eₚₑ/∂ log[KCl]) values are 37.49 and 87.38 mV/decade, respectively, for the anodic and cathodic redox processes. The values were considerably deviated from the ideal Nernstian value of 59 mV/decade and further suggest participation of nonstoichiometric alkali metal ion-coupled electron-transfer pathways such as 2K⁺/3e⁻ (slope ~40 mV/decade) and 3K⁺/2e⁻ (slope ~90 mV/decade), respectively, for the anodic and cathodic redox processes. This observation closely resembles with the nonstoichiometric response of the GCE/NiHCFe@f-MWCNT system with slope values of ~40 (2K⁺/3e⁻), and 120 mV/decade (2K⁺/e⁻) respectively, [27]. Over all the GMC matrix has some unique properties like CNT for the immobilization of NiHCFe units and for characteristic alkali metal ion-coupled electron-transfer behavior.

3.3. Electrocatalytic and Amperometric Sensing of Hydrazine.

The electrocatalytic activity of the GCE/NiHCFe@GMC towards oxidation of hydrazine was studied by cyclic voltammetry. Figure 5(a)(A–C) shows comparative CV responses of GCE/NiHCFe@GMC and GCE/GMC with 1 mM of hydrazine in a pH 7 PBS. As seen in Figure 5(a)(A) the GCE/NiHCFe@GMC yielded about 20 times enhancement in the oxidation current value and 500 mV reduction in the overpotential over the GCE/GMC (Figure 5(a)(C)) for the hydrazine oxidation reaction, and it is highlighting the efficient catalytic function of the GCE/NiHCFe@GMC in this work. Effect of hydrazine concentration was examined on the working electrode. Upon increasing the hydrazine concentration, a systematic increase in the anodic peak currents was noticed (Figure 5(b)). Plot of baseline corrected anodic peak current (iₚₐ) versus concentration of hydrazine was linear up to 1.0 mM, after that a plateau in the peak current response was noticed (Figure 5(c)). Calculated current sensitivity value for the hydrazine oxidation by CV was 15.86 μA/mM, which is about 15 times higher in sensitivity than that of the NiHCFe graphite [28] and sol-gel-derived NiHCFe-modified electrodes [20]. The linear response followed by the plateau observation depicts the electrocatalytic mechanism through the Michaelis-Menten type surface saturation kinetics with...
the following type of reaction steps (Scheme 2) [27], where the oxidized form of the NiHCFe, that is, -Ni$^{III}$-NC-Fe$^{III}$-CN-, first react with hydrazine and convert it to N$_2$ and in turn simultaneous formation of reduced form of the NiHCFe, that is, -Ni$^{II}$-NC-Fe$^{II}$-CN-. This reduced site gets back to the oxidized form by the operating redox potential and subsequently involved in the hydrazine oxidation in a cyclic manner (Scheme 2).

Amperometric $i$-$t$ detection of hydrazine on GCE/NiHCFe@GMC at an applied potential of 380 mV versus Ag/AgCl was displayed in Figure 6(a).A. Successive spike of 25 μM hydrazine results in systematic increase in current signal up to 220 μM of hydrazine with a current sensitivity of 7.37 nA/μM (Figure 6(b)). Control amperometric experiments with GCE/Ni@GMC and GCE/GMC showed about three and seven times decrease in the hydrazine current signals as in Figure 6(a)(B) and (C), respectively. Note that the GCE/NiHCFe has failed to show any such amperometric signal for hydrazine in this work (Figure 6(a)(D)), which may be due to absence of catalytic film on the surface as shown in Figure 2(B). Figure 6(b) display typical plots for the amperometric $i$-$t$ peak currents versus hydrazine concentrations. Calculated relative standard deviation (RSD) for detection of six successive spike of 25 μM hydrazine on GCE/
Figure 4: CV responses of GCE/NiHCFe@GMC at different (a) alkali metal ions and effect of (b) Na⁺ and (c) K⁺ concentrations at a scan rate of 50 mV/s. Figures 3(b) and 3(d) inset are typical $E_p$ versus log(alkali metal ion) plots.

Scheme 2: Reaction mechanism for the electrocatalytic oxidation of hydrazine on GCE/NiHCFe@GMC utilizing its A1/C1 redox couple.

NiHCFe@GMC is 1.97%. Calculated detection limit value ($S/N = 3$) is 23.2 nM. The detection limit value obtained here is around 26.5 times lesser than previous report with GCE/ NiHCFe@f-MWCNT [27], Ni(II)-Baicalein-MWCNT-Paste electrode [31], NiHCF-NP/CCE [32], and other chemically modified electrodes reported in the literature [11, 28, 33–38].
Figure 5: (a) CV responses of GCE/NiHCFe@GMC without and with 1 mM hydrazine (A and B) and GCE/GMC-modified electrode in presence of 1 mM hydrazine (C). (b) CV responses of GCE/NiHCFe@GMC with different concentration of hydrazine. (c) Typical calibration plot.

Observing such a low detection limit value with the GMC-modified electrode might be due to the low background current of the working electrode. Other control hydrazine oxidation experiments using GCE/Ni@GMC, GCE/GMC, and GCE resulted in relatively poor current signal values (Figures 6(a) and 6(b)). Interference effects due to various environmental and biological chemicals were also examined as in Figure 6(c). The GCE/NiHCFe@GMC has remarkable tolerance to the environmental chemicals (nitrite, citric acid, and oxalic acid), which were all often found to be seriously interfered during the hydrazine detection [39]. Meanwhile, feeble interference responses were observed with the biological samples: ascorbic acid, dopamine, and uric acid (Figure 6(d)). In the literature, Nafion was used as an overlayer coating to eliminate those interferences [39]. But no such specific extraneous treatment is required in the present case, which again confirms the promising electroanalytical performance of the present hybrid material.
3.4. Real-Sample Analysis. We have examined the applicability of GCE/NiHCFe@GMC for the determination of hydrazine in cigarette real sample by a standard addition method. Figure 7 shows typical amperometric $i$-$t$ signal for the analysis of hydrazine present in the cigarette smoke, which is dissolved in pH 7 PBS, using GCE/NiHCFe@GMC as a working electrode. The results are presented in Table 2. Amounts of net hydrazine content were found to be 13.2 ng/cigarette. This hydrazine content value is matching closer with the value of 31.5 ng/cigarette measured by derivatization-based gas chromatographic method previously [8]. The recovery of the spiked sample was found to be around 100%, indicating the appreciable suitability of present working electrode for the real-sample analysis.

Finally, in order to check the stability of the working electrode, CV was performed with the GCE/NiHCFe@GMC before and after the real sample. It is expected that various chemicals present in the real sample may deactivate the working electrode; in such a case marked decrease in the CV response will be expected. Interestingly, no such alteration in
Table 1: Comparison of hydrazine detection limit on various chemically modified electrodes.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Modified electrode</th>
<th>pH</th>
<th>Detection limit (μM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu–Pd screen-printed carbon electrodes</td>
<td>7.4</td>
<td>0.27</td>
<td>[11]</td>
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<tr>
<td>2</td>
<td>GCE/NiHCFe@f-MWCNT</td>
<td>7.0</td>
<td>0.62</td>
<td>[27]</td>
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<tr>
<td>3</td>
<td>NiHCFe-graphite electrode</td>
<td>7.0</td>
<td>0.10</td>
<td>[28]</td>
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<tr>
<td>4</td>
<td>Ni(II)-baicalein-MWCNT-paste electrode</td>
<td>13</td>
<td>0.80</td>
<td>[31]</td>
</tr>
<tr>
<td>5</td>
<td>NiHCFe-nanoparticle-carbon ceramic electrode</td>
<td>7.0</td>
<td>8.00</td>
<td>[32]</td>
</tr>
<tr>
<td>6</td>
<td>Indenedione -MWCNT-carbon ceramic electrode</td>
<td>7.0</td>
<td>0.29</td>
<td>[33]</td>
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<tr>
<td>7</td>
<td>GCE/ZnO-MWCNTs</td>
<td>7.0</td>
<td>0.18</td>
<td>[34]</td>
</tr>
<tr>
<td>8</td>
<td>GCE/Mn(II) complex-MWNTs</td>
<td>8.0</td>
<td>0.50</td>
<td>[35]</td>
</tr>
<tr>
<td>9</td>
<td>Co(II)complex-MWCNT-carbon paste electrode</td>
<td>7.0</td>
<td>0.10</td>
<td>[36]</td>
</tr>
<tr>
<td>10</td>
<td>GCE/CeHCFe-ordered mesoporous carbon</td>
<td>7.0</td>
<td>0.10</td>
<td>[37]</td>
</tr>
<tr>
<td>11</td>
<td>Polyethylenedioxy pyrrole/MWCNTs-Pd</td>
<td>7.4</td>
<td>0.04</td>
<td>[38]</td>
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<tr>
<td>12</td>
<td>GCE/NiHCFe@GMC</td>
<td>7.1</td>
<td>0.02</td>
<td>Present work</td>
</tr>
</tbody>
</table>

HCFe: hexacyanoferrate; MWCNT: multiwalled carbon nanotube; f-MWCNT: functionalized-MWCNT; GMC: graphitized mesoporous carbon; GCE: glassy carbon electrode.

Table 2: Hydrazine content analysis in cigarette smoke real sample using GCE/NiHCFe@GMC by amperometric $i$-$t$ at an applied potential of 0.38 V versus Ag/AgCl.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cigarette smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Samples</td>
</tr>
<tr>
<td>2</td>
<td>Linear equation</td>
</tr>
<tr>
<td>3</td>
<td>Regression</td>
</tr>
<tr>
<td>4</td>
<td>Original detect value (μM)</td>
</tr>
<tr>
<td>5</td>
<td>Spike (μM)</td>
</tr>
<tr>
<td>6</td>
<td>Detected after spike (μM)</td>
</tr>
<tr>
<td>7</td>
<td>Recovery (%)</td>
</tr>
</tbody>
</table>

the peak current and potential values was noticed, further evidencing the good stability and reproducibility of the working electrode even after the real-sample analysis.

4. Conclusions

In summary, a low-cost carbon material, GMC, was used as a matrix to immobilize NiHCFe (i.e., GCE/NiHCFe@GMC) and for sensitive and selective detection of hydrazine in a physiological solution. Alkali metal ion interaction with the NiHCFe@GMC was found to be in the stoichiometric and nonstoichiometric routes. The redox mechanism of the electrode follows surface-confined electron-transfer pathway. The modified hybrid electrode yielded about 20 times higher in the electrocatalytic oxidation of hydrazine than the unmodified electrode. Cyclic voltammetric and amperometric $i$-$t$ methods of detection of hydrazine showed calibration plots which were linear up to 1 mM and 220 μM, respectively. Calculated detection limit value for the hydrazine by the amperometric method was 23.2 nM, which was about 26.5 times higher than the NiHCFe-functionalized multiwalled carbon nanotube hybrid electrode reported by our group recently. Detection of hydrazine in cigarette smoke sample was successfully demonstrated with appreciable recovery values.

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