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Highly Sensitive Determination of Chromium (VI) Based on Reduced Graphene Oxide / Polyaniline - Nafion Composite Modified Electrode

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ABSTRACT

A Reduced Graphene oxide, Polyaniline protected Reduced Graphene Oxide and Reduced Graphene oxide-Polyaniline / Nafion modified glassy carbon (RGO-PANI / Nf / GCE) electrode was prepared and characterized by UV-Vis, FT-IR, XRD and FESEM with EDX Spectrum. The Reduced Graphene oxide-Polyaniline / Nafion (RGO-PANI/Nf) composite for chromium (VI) electrochemical sensing is described. The electrochemical behaviour of Cr (VI) at the Reduced Graphene oxide-Polyaniline / Nafion composite modified glassy carbon electrode (GCE) was investigated by differential pulse voltammetric method. The results showed that the incorporation of polyaniline with graphene significantly enhanced the electrochemical reactivity and voltammetric response of Cr (VI). In addition, Nafion acts as an effective solubilizing agent and antifouling coating in the fabrication of the modified electrode. This electrochemical sensor exhibits excellent analytical performance for Cr (VI) detection at physiological pH with detection limit of 2.1×10^{-7} M, linear range of 1–100 μ M and reproducibility of 3.6% relative standard deviation.

Keywords: Graphene oxide, Polyaniline, Nafion, Chromium, DPV, GCE

INTRODUCTION

Heavy metal ions are paid more attention in environmental, toxicological, pharmaceutical, and biomedical analysis point of view [1–3]. Among those, the detection of chromium is of particular interest owing to the high toxicity of chromium (VI) ions. The detection of chromium species is a challenging task because of the different possible oxidation states of the element. The most common valences are 0, +II, +III, and +VI. The two environmentally relevant valence states of chromium, namely, Cr(III) and Cr(VI), have a contrasting impact on environment and health. Trivalent chromium is relatively harmless, plays an essential role in biological processes, and is related to human glucose tolerance [4], whereas hexavalent chromium is about 100 times more carcinogenic and toxic [5] because of its high oxidation potential and is limited in groundwater by WHO provisional guideline value of 0.05 mg L^{-1} (50 ppb) [6]. The main sources of anthropogenic chromium pollution in ground water are plating industries, cooling towers, timber treatment [7], leather tanning, wood preservation, and steel manufacturing [8]. The major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum, and local effects in the lungs [9]. Various techniques for the determination of Chromium have been developed in recent years. The common analytical methods include separation of Chromium by high-performance liquid chromatography (HPLC), Extraction and pre-concentration step using ion exchange or chelating resin. This pretreatment often coupled with detection systems such as spectrofluorometry [10], spectrophotometry [11,12], chemiluminescence [13], atomic absorption spectrometry (AAS) [14–15], inductively coupled plasma atomic emission spectrometry (ICP-AES) [16] and inductively coupled plasma mass spectrometry (ICP-MS) [17]. However, these pretreatment and detection processes do not satisfy all requirements for routine analysis, mainly because of their complicated procedures, time consumption or the high cost of instrumentations. Electrochemical methods, in particular voltammetry, have important advantages for the determination of metals at trace concentrations such as high sensitivity and low detection limit, relative simplicity, low cost of equipment and portable option [18,19]. Voltammetric methods have

been described in the literature for the detection of Cr(VI) using metallic nanoparticles modified carbon screen-printed electrodes [20], pyridinium-based sol-gel film [21], self-assembled monolayer [22], and Graphene based modified electrodes [23,24]. Graphene, a single layer of sp² hybridized carbon atoms packed into a dense honeycomb two-dimensional lattice, has attracted tremendous attention from both experimental and theoretical scientific communities since it was experimentally produced in 2004 [25-27]. Graphene-based materials hold great promise in fabricating enhanced electrochemical sensing platforms. However, graphene-based nanocomposite film has never been used for the determination of Cr(VI). Herein, we report on an ultrasensitive Cr(VI) sensor by using nanocomposite film of polyaniline (PANI) and graphene as the powerful platform. Uniform PANI were homogeneously distributed onto the graphene nanosheet matrix, constructing a monodispersed PANI based ensemble. It is worth noting that the as-prepared composite matrix in this work combines the advantages of the graphene nanosheets (unique electrical conductivity and enlarged active surface area) together with PANI (extraordinary catalytic activity and good conductivity). This should greatly facilitate the rapid, stable and sensitive measurement of Cr(VI). The performance of this novel platform for voltammetric detection of Cr(VI) is investigated in detail. Encouragingly, such a nanostructured composite film offers a remarkably improved sensitivity and selectivity and exhibits fine applicability for the detection of Cr(VI).

MATERIALS AND METHODS

2.1. Chemical reagents

Graphite powder, Sulfuric acid, hydrochloric acid (98%), ethanol, hydrogen peroxide (30%) Potassium permanganate, hydrazine monohydrate (35%), Aniline monomer, ammonium peroxydisulfate, Sodium nitrate and Nafion were purchased from Precision, India. All reagent were of analytical reagent grade and were used without further purification. All the reagents were prepared using Milli- Q water.

2.2. Synthesis of Graphene Oxide

Graphene oxide was prepared from natural graphite powder using modified Hummers Jr. and Offeman method [25] as follows. In a typical synthesis, 1 g of graphite and 1 g of NaNO₃ were mixed with 46mL of H₂SO₄ (98%) in a 250mL flask in an ice bath. To it, 6 g of KMnO₄ was slowly added at below 20°C with vigorous stirring. The resulting mixture was stirred at room temperature for 1 h, diluted with 70mL of water, and stirred at 95°C for 2 h. Then, the mixture was further diluted with 100mL of water and deoxidized with 7mL of H₂O₂ (30%). Finally, the product formed in the solution was separated out by centrifugation at 7000 rpm and then repeatedly washed with 600mL of water for six times until the pH of supernatant was neutral. The graphene oxide (gray powder) was obtained by drying the product in vacuum at 60°C for 24h.

2.3. Reduction of GO

In a typical experiment, 3.5 mL of ammonia solution (25%) and 0.5 mL of hydrazine monohydrate (99%) were added into 500 mL of diluted GO dispersion (1.5 mg/mL) and then the mixture was heated at 95°C for 2 h under vigorous stirring. Once the reaction is completed, the reduced graphene oxide (RGO) were collected by filtration as a black powder, washed with copious amounts of deionized water.

2.4. Preparation of Polyaniline protected Reduced Graphene Oxide

In a typical synthesis of RGO-PANI, aniline (1.05 mmol) and RGO(100 mg) were dispersed in 40 mL of 0.2 M HCl aqueous solution under ultrasonication. A fresh solution of ammonium peroxydisulfate (APS, 0.54 mmol) in 20 mL of 0.2 M HCl solution was rapidly transferred to the above solution containing aniline and RGO. The polymerization reaction was carried out for 12 h at room temperature without any disturbance. The dark green precipitate was filtered off, washed with deionized water and ethanol several times, and dried at 80°C for 24 h. The RGO-PANI synthesized. Herein, the pure PANI was synthesized chemically in the absence of RGO via the similar procedure above for comparison.

2.5. Fabrication of the modified electrode

Bare glassy carbon (GC) electrode was used for the modification. Before the modification the electrode was polished mechanically by slurry of aluminium oxide (Al₂O₃) powder with a particle diameter of 0.05µm, then washed with deionized water and ethanol in sequence before use. Then as-prepared GO-PANI nanocomposite was dispersed in ethanol containing 2.5% (V/V) Nafion with ultrasonication for 1 h to get a homogenous suspension (1mgmL⁻¹). Then, 5µL of the suspension was dropped onto the surface of freshly polished glassy carbon electrode (GCE) and dried at room temperature, resulting in the Nafion / GO-PANI modified GCE (Nafion/ GO-PANI /GCE).

2.6. Instruments

The phase and the crystallographic structure were identified by X-ray diffraction (XRD, Philips X'Pert Pro, Cu-K α : $\lambda = 0.1540598$ nm). The particle size and morphology of the products were studied by FE-Scanning Electron Microscopy (FE-SEM) (HITACHI SU6600 SEM). FTIR spectra were recorded for studying the functional groups using KBr disks on a Shimadzu affinity spectrophotometer.

2.6. Electrochemical setup

Electrochemical measurements were performed using CHI 660C model using a three electrode type electrochemical cell. A three-electrode system was employed with a SCE-sat. KCl as reference electrode, a platinum wire as counter electrode and RGO-PANI /Nafion modified GCE as working electrode respectively.

RESULTS AND DISCUSSION

3.1. FT-IR Characterization

The FTIR spectra of GO, RGO, PANI and PANI-RGO are shown in Fig. 1. For the GO, the characteristic bands at 1061, 1394, 1620 and 1725 cm^{-1} were identified as C-O-C, O-H (C-OH), C=C, C=O (-COOH), and O-H (H_2O), respectively [21]. These features indicated that graphene oxide was heavily oxidized and consisted of -OH and other oxygen-containing groups. After GO was reduced, the C=O vibration band located at 1725 cm^{-1} disappeared, but a new shoulder peak located at 1713 cm^{-1} was observed, suggesting that GO had undergone partial reduction to RGO during the hydrothermal process [27]. For the pure PANI, the peaks at 1560, 1450, 1290, 1110 and 790 cm^{-1} were attributed to C=C stretching of the quinonoid ring, benzenoid ring, the C-N stretching of secondary aromatic, C-H in-plane bending and CH out-of-plane bending modes, respectively [21]. In the PANI-RGO, the peak at 1700 cm^{-1} (GO) of the C=O stretching vibration was shifted to 1710 cm^{-1} due to the formation of the amide bond in the hybrid, and the C=C stretching intensity ratio of quinonoid ring (1540 cm^{-1}) was improved in the FTIR spectrum of the as-prepared composite. It indicated that the structure of the quinonoid ring was promoted and stabilized by the chemical bonds between residual oxygen-contained functional group of the RGO (O = C-OH) and amino-group (-NH₂) of PANI in the PANI-RGO composite [21].

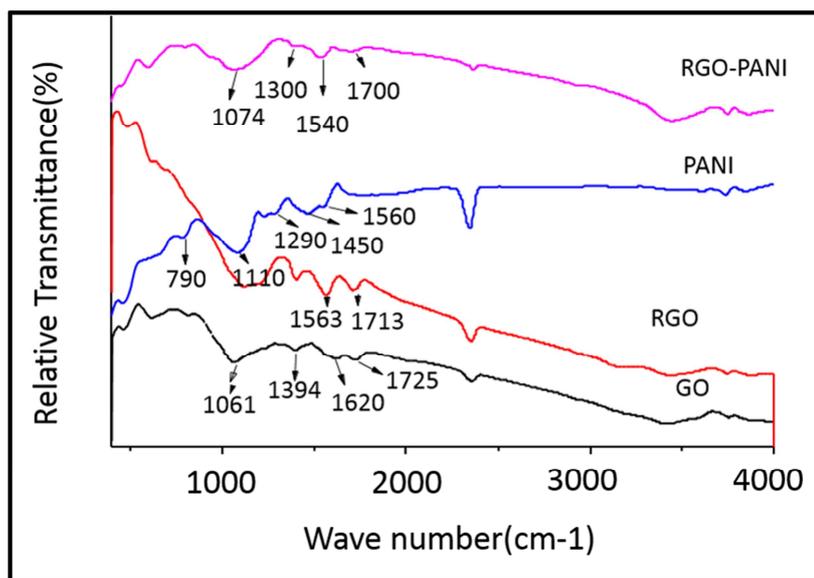


Fig. 1 FT-IR spectrum of GO, RGO and RGO/PANI

3.2. UV Characterization:

Typical UV-vis spectra of GO, RGO, RGO-PANI are shown in Fig. 2. The UV-VIS spectra of GO exhibits a maximum absorption peak at about 223 nm, corresponding to π - π^* transition of aromatic C-C bonds. The absorption peak for reduced GO had red shifted to 270 nm. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO

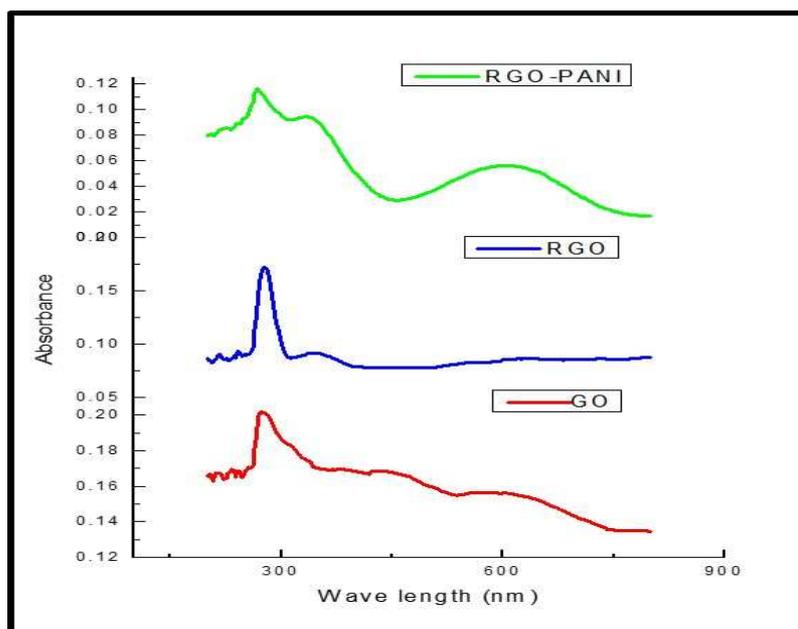


Fig. 2 UV- Vis spectrum of GO, RGO and RGO/PANI

3.3 XRD Characterization:

Fig. 3 showed the XRD spectra of graphite, GO, RGO and PANI - RGO. The graphite showed very strong peak at 26.5° . For the GO, the introduction of oxygen-containing groups disrupted the carbon hexagonal plane and the interlayer spacing was increased from 0.34 nm to 0.77 nm by weakening the van der Waals forces between the layers [29]. Therefore, the characteristic graphitic plane at $2\theta = 26.5^\circ$ shifted to 11.4° . After the reduction to RGO, the peak at $2\theta = 11.4^\circ$ disappeared and two new peaks appeared at 17.8° and 24.6° , and the peak was broadened, which indicated that the uncrystallized nature arose due to the poor ordering in the stacking direction [29]. Besides, for the nanocomposite of PANI-RGO, the peak at $2\theta = 11.4^\circ$ also disappeared and two peaks at 17.4° and 25.1° appeared, suggesting that a significant portion of GO was reduced and exfoliated during covalent grafting. Broadening of the peak indicated the amorphous nature of the PANI-RGO due to the poor ordering in the stacking direction

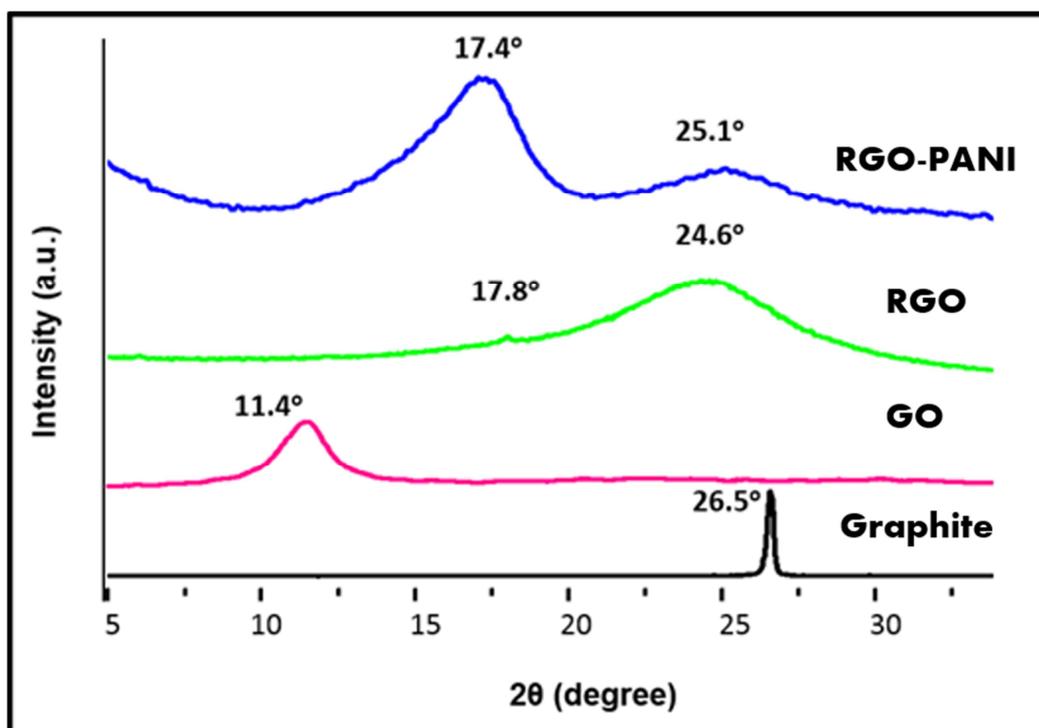


Fig. 3 X-ray diffraction spectrum of GO, RGO and RGO/PANI

3.4. FESEM

The morphologies of the as-obtained RGO, PANI and PANI-RGO hybrid were further studied by FESEM with EDX. The results are shown in Fig. 4. Fig. 4A displayed the SEM image of the RGO film, in which a large area thin film with wrinkle was observed, indicating RGO had been synthesized. Fig. 2B shows the SEM image of PANI showed that the PANI has a meshed uniform fibrous structure. From the higher magnification image (inset of Fig. 4B), it could be seen that network contained high pore volume in the microporous structure. When RGO was combined with PANI, some obvious crumpled structure in accordance with the characteristics of RGO were observed, and became much more rough and shaggy compared with RGO sheets, and the sheet was easily folded to form overlapped structures (Fig. 4C). At the same time, the PANI exhibited same morphology as that shown in Fig. 4B, suggesting that the PANI had been coated well with RGO.

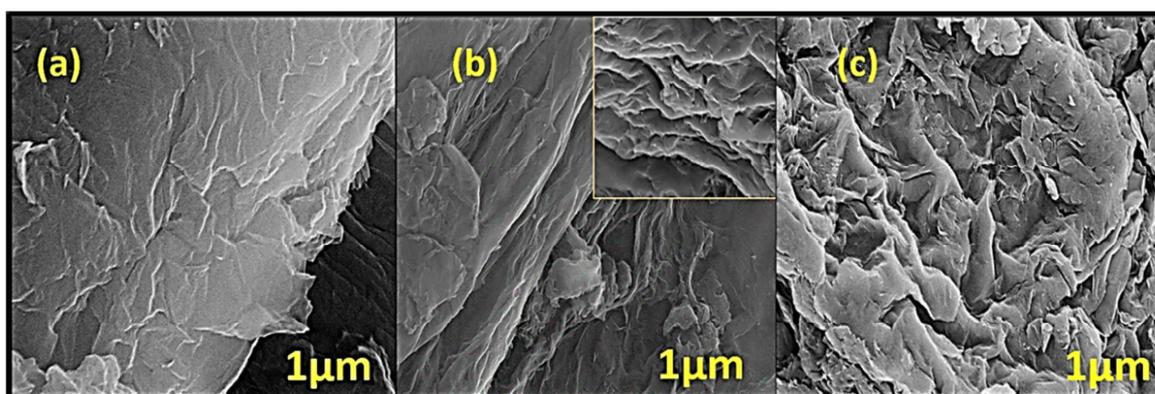


Fig.4 FESEM of (a) RGO (b) PANI and (c) RGO/PANI

3.5. Electrochemical Studies

3.5.1. Effect of Electrolyte

An initial study of the reduction of Cr(VI) was carried out using cyclic voltammetry at glassy carbon (GC) electrode materials. When bare GC electrode was tested by running a CV in two different electrolytes, namely, 0.1 M and 0.01 M HCl. To choose the pH of the electrolyte, CVs were run in different electrolytes, namely, 0.1 M and 0.01 M HCl. Figure 3 shows the corresponding cyclic voltammetry curves plotted as current versus potential obtained for 0.1 M HCl and 0.01 M HCl electrolyte using bare GC electrode at a scan rate of 100 mVs⁻¹. There were not any peaks except for the peak at higher potentials. The CV for 0.01 M HCl showed a large capacitive current and, in this regard, the detection of Cr(VI) ions will be uncertain. From the figure, it can be seen that 0.1 M HCl gave good response and hence 0.1 M HCl was taken as the standard electrolyte system.

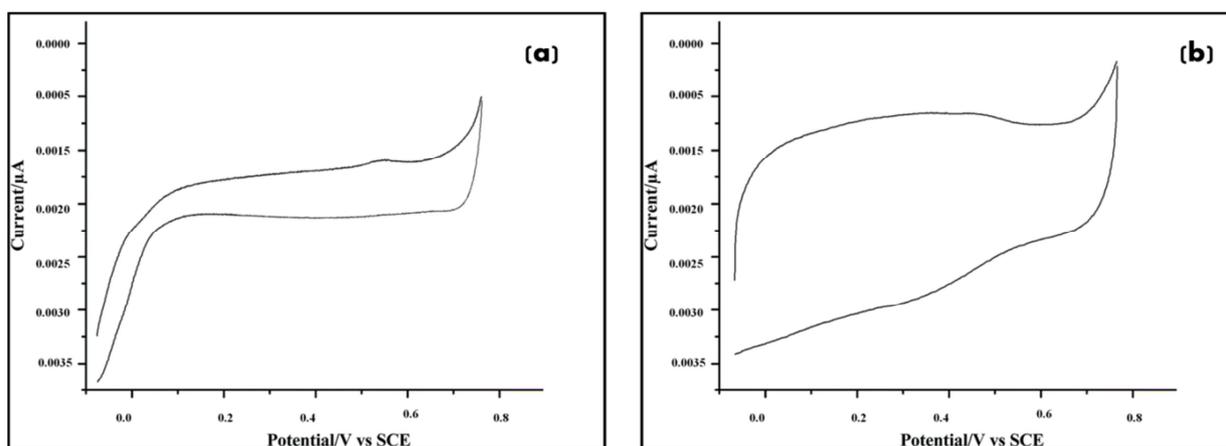


Figure 5: Voltammetric responses of bare glassy carbon (GC) electrode in different electrolytes: (a) 0.1M HCl and (b) 0.01M HCl, respectively (scan rate = 100mVs⁻¹)

3.5.2. Effect of pH

HCl solutions with pH ranging from pH 1.0–3.0 were used as supporting electrolyte for cyclic voltammetry experiments of Cr(VI). Fig. 8 showed the variation of reduction peak current of 10 mmolL⁻¹ Cr(VI) at the RGO-PANI / Nf / GCE in the HCl solutions with different pH values. As shown in Fig. 8, the current response of Cr(VI) increased as the pH increased from 1.0 to 2.0 and then decreased as the pH increased from 2.0 to 3.0. The maximum

peak current with a well-defined voltammetric curve was obtained at pH 2.0. It proves that the response of Cr(VI) at RGO-PANI / Nf / GCE is highly pH dependent.

3.5.3. Effect of Scan rate

The voltammetric responses of 50 μM chromium in 0.1 M HCl at various scan rates of 10 mV, 30 mV, 50 mV, 200 mV, and 400 mV were examined by cyclic voltammetry using Nafion/RGO-PANI modified GC electrode as shown in Figure 7. These reveal process with a peak potential at +0.46 V (100 mVs⁻¹), which was found to shift up to +0.4 V (400 mVs⁻¹) as the scan rate increases. The fact that peak potential is dependent on scan rate.

3.5.4. Electrochemical Detection of Cr (VI) Using Bare GC Electrode.

Before probing the role Nafion/RGO-PANI modified electrode, bare GC electrode was checked for Cr(VI) ions reaction analysis.. Voltammetry plotted as current versus potential in 0.1 M HCl electrolyte containing 200 μM Cr(VI) using bare glassy carbon (GC) electrode at a scan rate of 50 mVs⁻¹. It can be seen that the response of GC electrode to Cr(VI) in 0.1 M HCl gave a well-defined reduction peak at +0.314 V. The shape of the voltammogram might be preliminarily attributed to an electrochemically reversible process, whilst the absence of corresponding oxidation peak in the potential range studied indicates a chemically irreversible reaction.

3.5.5. Electrochemical Detection of Cr(VI) on Nafion/RGO-PANI Modified GCE.

Figure 6 shows the corresponding cyclic voltammetric run in 0.1 M HCl containing 200 μM Cr(VI) using Nafion/RGO-PANI Modified GC Electrode at a scan rate of 50 mVs⁻¹. As can be seen, the response obtained at the modified GC electrode consists of a peak at +0.46 V. Comparing both modified and unmodified electrodes, the peak potential is quite good at the modified GC electrode which increases the sensitivity of hexavalent chromium ions. A comparison of unmodified and Nafion/RGO-PANI Modified GC Electrode (Figures 4 and 6) reveals that the reduction is enhanced in the presence of graphene/GC modified electrode surfaces. Compared to the bare GC electrode, the nanoparticle-modified electrodes exhibited typical voltammetric response for Cr(VI). The Nafion/RGO-PANI Modified GC Electrode shows well defined voltammetric peaks for Cr(VI) at 0.4 V. The voltammetric response obtained is ascribed to the three-electron reduction of Cr(VI) to Cr(III). The unmodified GC electrode shows a reduction peak at 0.3 V. The shift in the reduction potential and increase in the peak current with respect to the unmodified electrode imply that the nanosized particles on graphene matrix efficiently catalyse the reduction of Cr(VI).

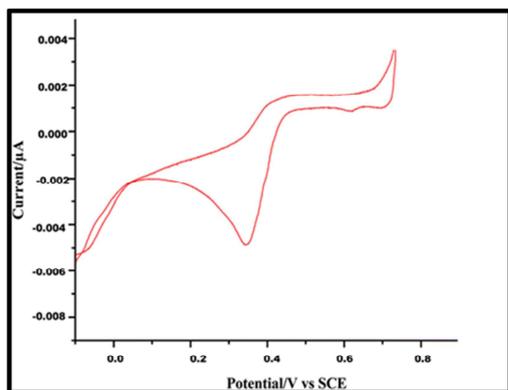


Figure 6: Cyclic voltammograms detailing response bare GC electrode to 200 μM Cr(VI) in 0.1 M HCl (scan rate = 50 mVs⁻¹).

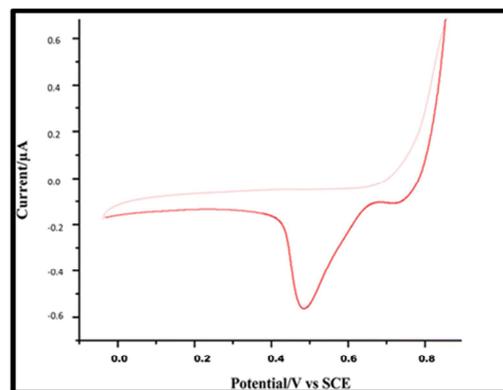


Figure:7 Cyclic voltammogram response of a Nafion/RGO-PANI Modified GC Electrode 200 μM Cr(VI) in 0.1 M HCl (scan rate = 50 mVs⁻¹).

3.5.6. Effect of concentration

In order to further validate the diffusional nature and, in particular, to test the analytical applicability of the reduction process, the response of RGO-PANI / Nf / GC electrode to increasing additions of Cr(VI) (5–800 μM) in 0.1 M HCl was examined. A plot of the change of reduction peak current as a function of hexavalent chromium added to the solution was found to be linear in the concentration range studied (slope = 1.313 and $R^2 = 0.9756$) consistent with a diffusion-controlled reaction (see Figure 8).

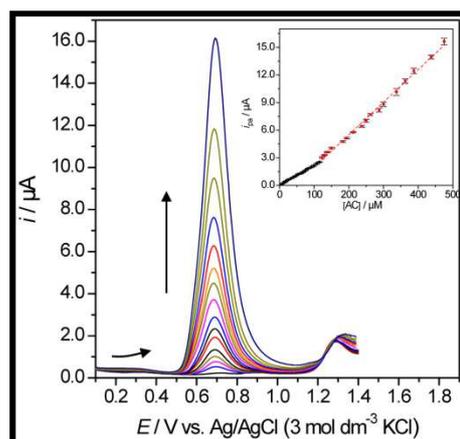


Figure 8: Cyclic voltammograms detailing the response to different scan rates ($10\text{--}400\text{ mVs}^{-1}$) for the solution containing $50\text{ }\mu\text{M Cr(VI)}$ in 0.1 M HCl at a RGO-PANI / Nf modified GC electrode

CONCLUSION

The reduction of chromium was examined at modified and unmodified GC electrodes. It was found that modified GC electrode (RGO-PANI / Nf modified GC electrode) provided good voltammetric responses towards the addition of Cr(VI) in the electrolyte solutions. It was also verified that, in the presence of graphene-/PANI based electrodes, the reduction process occurs at more positive potential when compared with that of unmodified GC electrode. The response of the electrode to addition of chromium was found to be independent of environmental interferences, such as Ni, Cu and Cr(III).

This investigation proved that the composites are good materials for electrochemical sensing of chromium ions.

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