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Carbon Nano Onions–Polystyrene Composite for Sensing S-Containing Amino Acids

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Abstract: A carbon nano-onions (CNOs)–polystyrene (PS) composite-based Pt electrode was used for the voltammetric detection of cysteine (Cys) and methionine (Met). The electrochemical behaviors of Cys and Met were analyzed with Cyclic Voltammetry (CV) and Differential Pulse (DP) Voltammetry at different pHs. The modified CNOs–PS/Pt electrode shows an oxidation peak at +0.4V for Cys and +0.8V for Met, respectively. Admirable sensitivity, easy fabrication, and reproducible performance make the proposed electrode well functional and useful for the qualitative and quantitative detection of sulphur-containing amino acids.

1. Introduction

Nanomaterials are used extensively as sensors and have seen pronounced development in recent years. After their combination with current electroanalytical methods, these nanomaterials gain excellent electrocatalytic properties, which can be used in demonstrating the electrochemical performance and sensing of electroactive compounds [1,2]. Carbon nano-materials, such as nanotubes, nanowires, nanoparticles, and graphene, are widely used because they have unique physical and chemical properties that can be used to modify the electrode in its use as an electrochemical sensor [3,4].

The detection of amino acids is extremely important, as they play a very important role in the construction of biological molecules because they are vital ingredients and, hence, the production of accurate and selective detection using a new method is of great importance [5–7]. However, it is not easy to detect amino acids because of the absence of natural chromophores for photometric detection. However, it is a very important assignment to determine these amino acids, particularly in different fields, such as biotechnology, food, and other related industries [8–10]. A number of clinical problem origins are due to the deficiency of cysteine(Cys) as it plays very significant role in biological systems [11–13]. In different biological media, cystine, which is the oxidized product of Cys, assists as a prototype for the thiol group of proteins [14]. Another S-containing amino acid methionine (Met), is also an important amino acid, as its deficiency causes dementia, fatty liver, slow growth, and edema problems. Therefore, the selective, sensitive, and low-cost determination of Cys and Met are very significant in the field of health diagnostics.

Carbon nano-materials, such as carbon nanotubes (CNTs), mesoporous carbon, and boron-doped diamond, and several modified electrodes with an enhanced response for electrochemical investigation,

have been described [11,15,16]. Different kinds of amino acids are sensed by using carbon nanotube-modified electrodes [17–20]. Ziyatdinova and co-workers showed that L-Cys and L-Met are electrochemically active on the multiwalled carbon nanotube (MWCNT)-based glassy carbon (GC) electrode [21]. Moreover, an electrode modified with carbon paste was used for the detection of Cys [22–24]. The use of the modified GC electrode is very common to detect Cys and Met. The GC electrode, modified with catechol [7,25] and gold nanoparticle embedded pyrimidine [26], was used to detect Cys and Met. Moreover, a carbon electrode, modified by using cyclotricatechylene, was used for the selective detection of Cys [27]. Other nanomaterials, such as ZnO nanorods, modified the carbon paste electrode [28], while the graphene-oxide modified screen printed carbon electrode [29] and Ru–Pt bimetallic monolayer on a nano-porous gold film electrode [30] were used to detect Met. Furthermore, different skills, such as those of the glucose/O_2-based biofuel cell [31], the fluorescence quenching process [32] and the organic field-effect transistor [33], are used to detect Cys and Met. In 2011, our lab group reported a method to detect a trace amount of SO_2 and H_2S by using a MWCNT-modified Pt electrode [11]. Besides, other materials, such as nano carbon composites, are used for the detection of toxic materials in food coloring [34], and graphitic nanorods for the detection of DNA [35] were used. For the detection of trinitrophenol (TNT), N and P co-doped fluorescent carbon dots were used [36]. The wsCNOs interact with dsDNA to form various self-assembled structures [37]. Along with that, we have prepared nanotubes from single amino acids (tryptophan and tyrosine) using self-assembly techniques [38]. These results give us a clue that wsCNOs can be used as a sensor for the detection of biochemical compounds.

The present work describes a convenient method for the determination of Cys and Met by using a composite of CNOs–polymer Pt electrode. Factors, such as the effect of percentage composition of the modified electrode, pH, and supporting the electrolyte, are considered to improve the sensitivity of the test. The experimental data show that the CNOs–polymer composite Pt sensor is highly sensitive to Cys and Met amino acids. As far as we know, this is the first report which shows that CNOs–PS composite-based Pt electrodes can be used for electrochemical detection of amino acids.

## 2. Experimental Details

2.1. Materials

Analytical grade reagents were purchased from Merck-India and used without further purification. Water was used from a Millipore Milli-Q system (conductivity $\leq 0.1 \mu Scm^{-1}$). The CNOs were synthesized using the method described earlier [39–41].

2.2. Instrumentation

For the imagining of the size and morphology, we used the Quanta 20 KV Field Emission Scanning Electron Microscope (FE-SEM) (SUPRA), equipped with an energy dispersive X-ray (EDX).

The morphology of the CNOs was observed by using a Tecnai 20 G2 200 kV, STWIN model, High Resolution Transmission Electron Microscope (HRTEM).

DP Voltammograms and Cyclic Voltammograms were recorded with BASi Epsilon, EC, Bioanalytical Systems Inc., West Lafayette, IN, USA. The experimental setup is shown below in Figure 1. The electrochemical cell consisted of three electrodes, Ag/AgCl as a reference electrode, a 6 cm modified Pt wire as the working electrode, and a platinum auxiliary electrode. All electrochemical experiments were carried out under an argon atmosphere at 298K. Potentials are ascribed against internal ferrocene (Fc) and are testified relative to the Ag/AgCl electrode ($E_{1/2}(Fc^+/Fc)$ 0.459 V vs. Ag/AgCl electrode). pH measurements were carried out on an ISFET pH meter (Delta Track, Pleasanton, CA 94566, USA). Sample solutions were prepared in Millipore water.
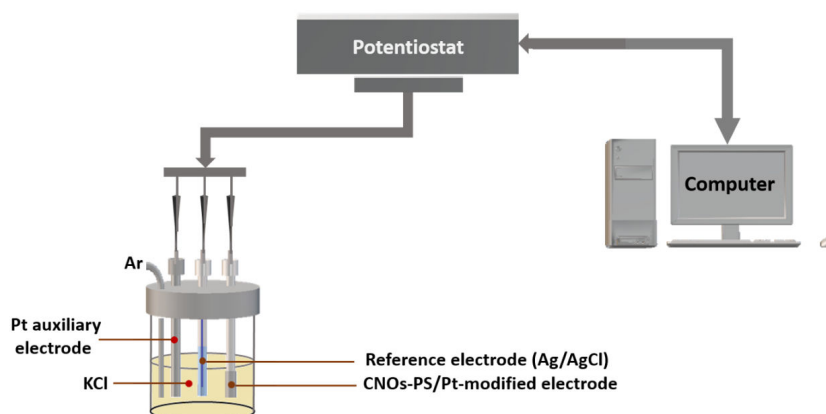
Figure 1. Experimental setup to detect Cys and Met.

2.3. Modification of Electrode for Amino Acid Sensing

For the preparation of CNOs–polymer composite Pt sensor, 100mg of polystyrene was dissolved in 5mL DCM and was then dispersed into a known amount of CNOs by ultrasonication for 15 min. This homogeneous black suspension was allowed to stand with frequent stirring until a concentrate jelly-type mass was obtained. The amount of CNOs was varied from 1 to 5% and 10% on the basis of the polystyrene used. The Pt wire was taken, having a length of 6 cm and diameter of 0.1 cm. Then a 2 cm portion of this Pt wire was dipped in a black suspension of CNOs–PS several times, allowing for the deposition of it on the Pt wire. The wire was then kept at room temperature to allow for the evaporation of the solvent.

By using analytical grade reagents and purified water, we prepared different electrolyte solutions by using different compositions, as shown in Table 1. From these buffer solutions, different concentrations of Cys and Met solutions were prepared.

Table 1. Preparation of buffer solutions.

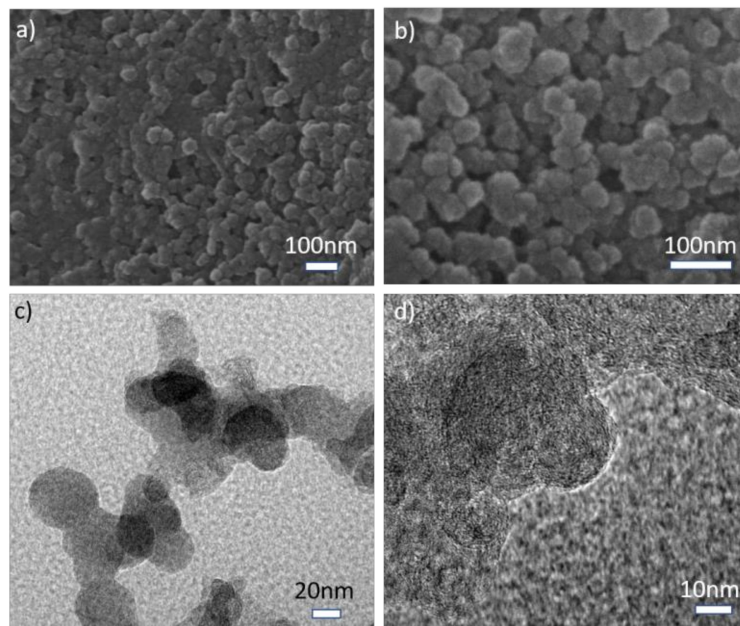| pH	Composition
1	HCl + KCl
2	HCl + KCl
3	Acetic acid + Sodium acetate
4	Acetic acid + Sodium acetate
5	Acetic acid + Sodium acetate
6	Acetic acid + Sodium acetate
7	Disodium hydrogen phosphate + HCl

2.4. Cys Detection in Green Beans

To 3 gm crushed green beans, 25 mL (pH1) buffer solution was added, and the solution was stirred for 15 min. The mixture was filtered and the filtrate was subjected to the electrochemical sensing of Cys using the modified CNO–PS/Pt electrode.

**3. Result and Discussion**

3.1. Structural Characterization

The morphology of synthesized CNOs was investigated by SEM and HRTEM techniques. Figure 2a,b exhibits the SEM images of CNOs. These images show the spherical morphology of CNOs with diameters varying from 20 to 50 nm. It is corroborated by the HRTEM analysis of CNOs, as shown in Figure 2c,d. The HRTEM image, as shown in Figure 2d, reveals that these spheres consist of layers and hence the onion-type nature of the structure is concluded.

Figure 2. The micrographs of CNOs (**a**,**b**) are SEM images; (**c**,**d**) are HRTEM images.

3.2. Electrochemical Behavior of CNOs–PS/Pt-Modified Electrode

The Cyclic voltammograms of Cys and Met at the CNOs–PS/Pt-modified electrode with a different composition ratio of PS and CNOs in 0.5 M KCl solution are revealed in Figure 3a,c. During the deposition, the amount of PS was kept constant (100 mg) and the amount of CNOs was varied from 1 to 5 and 10 mg for determining both the amino acids.
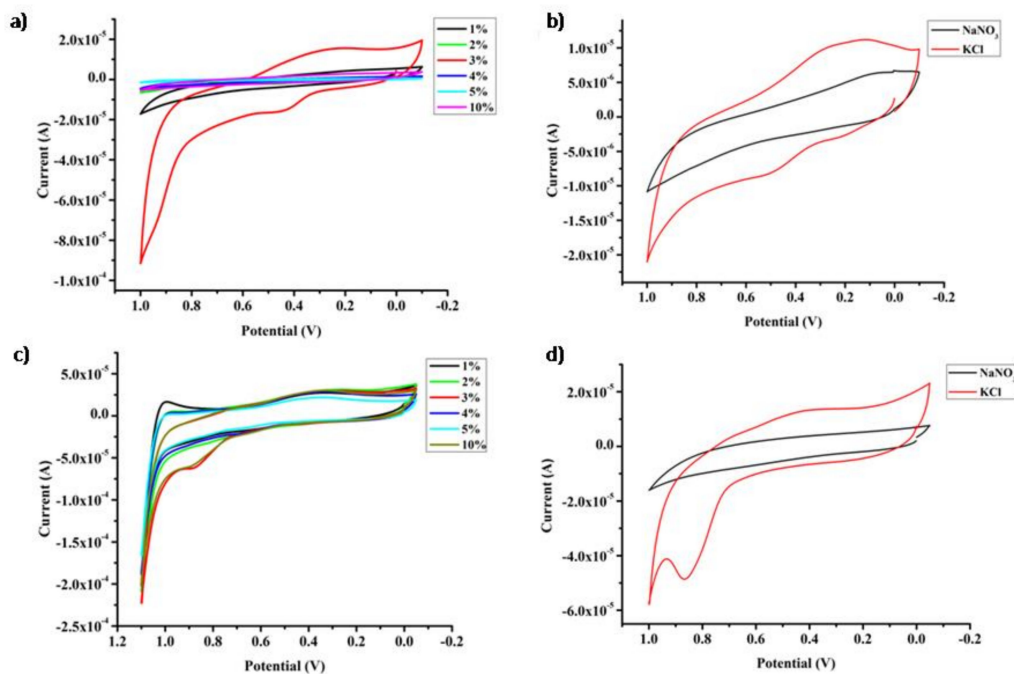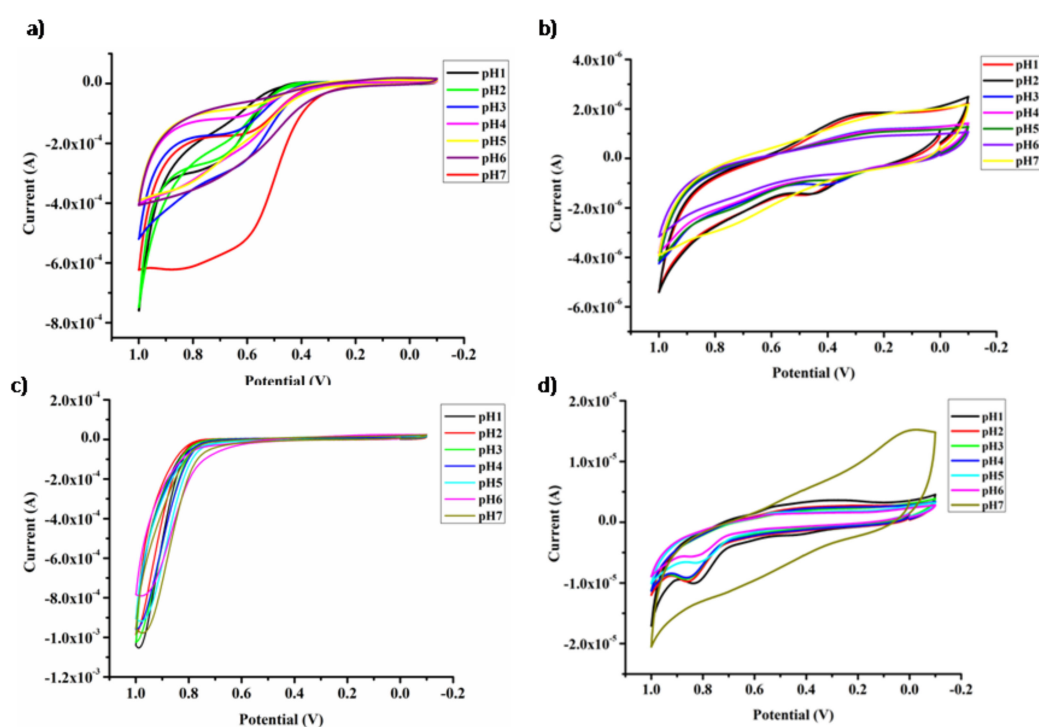

Figure 3. The Cyclic voltammogram of different percent composition of CNO in CNOs–PS/Pt-modified electrode in 0.5 M KCl solution in the presence of 10^{-2} Mat at a scan rate of 0.1 V/s (**a**) Cys, (**c**) Met; (**b**,**d**) are the Cyclic voltammogram of different supporting electrolyte for Cys and Met, respectively.

The oxidation peak at +0.43 V and +0.86 V for Cys and Met, respectively, showed a slight difference at a different proportion in the composition of CNOs–PS, but at the composition of 3 mg CNOs and 100 mg PS, the composite exhibits the best response to Cys, as well as Met, and this ratio was selected for further studies.

The effect of the supporting electrolyte was investigated in basic and neutral electrolytes (e.g., NaNO$_3$ and KCl), as shown in Figure 3b,d. High current peaks were obtained using 0.5M KCl as a supporting electrolyte. So, for further study, we used 0.5M KCl as a supporting electrolyte.

3.3. Effect of pH

To optimize the pH of the solution for Cys and Met detection, the effect of pH on the response of current was investigated in a buffered solution containing 0.5 M KCl. It was observed from the Cyclic Voltammogram that the electrode showed the best response in the pH range of 1 and 2 and low response in the range of pH 3 and 4 for Cys, as shown in Figure 4b.The best response for Met was observed in the pH range 1to 4 and low in the pH range 5 and 6 at a concentration of 10^{-2} M, as shown in Figure 4d. We also checked the detection of these solutions by using the bare Pt electrode only. It shows a broad oxidation peak for Cys and the actual position could not be located, as shown in Figure 4a,whereas, no oxidation peak was observed for Met in similar conditions, as shown in Figure 4c.
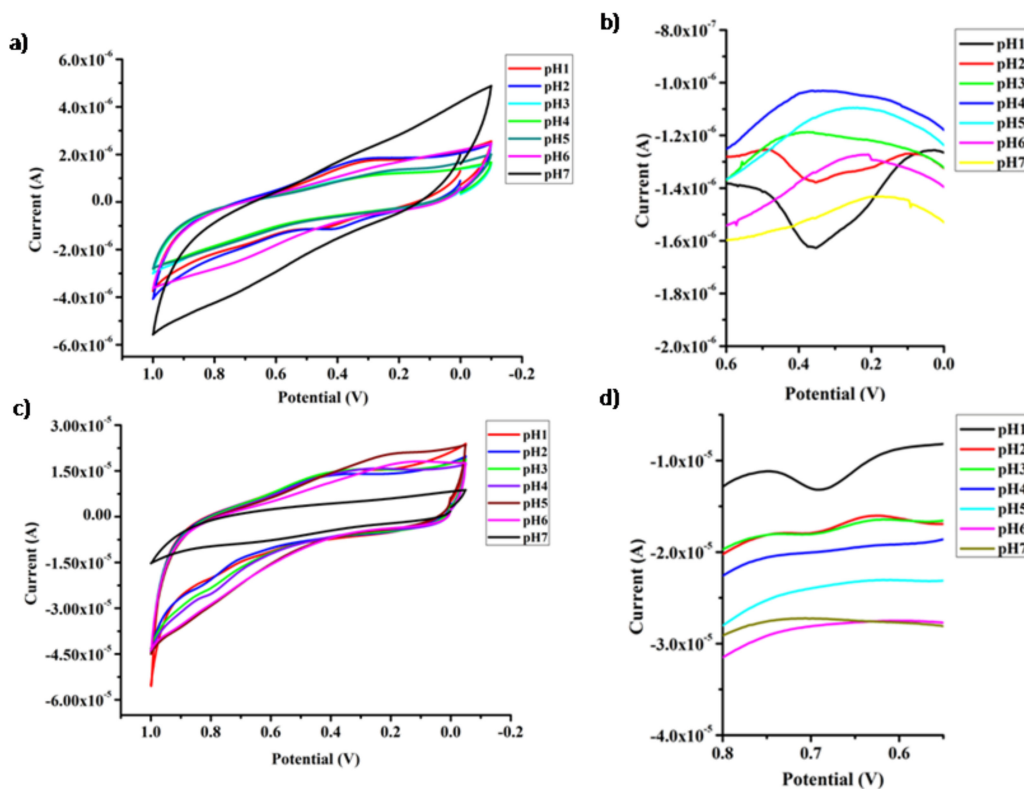

Figure 4. Cyclic voltammogram of bare Pt electrode as a working electrode for (**a**) Cys (10^{-2}M) and (**c**) Met (10^{-2} M) at different pH; (**b**,**d**) are Cyclic voltammogram of 3% CNOs–PS/Pt electrode as a working electrode for Cys and Met, respectively, at a scan rate of 0.1 V/s.

DP Voltammetry was also used to investigate the effect of pH on the electrochemical responses. Figure 5a,b shows the differential pulse voltammogram for Cys and Met, respectively. It is clearly showing the detection of Cys and Met at high pH range (pH 1 and 2). Further electrode responses were observed in 10^{-3} M concentrations of both Cys and Met. Figure 6a,c shows the cyclic voltammogram for Cys and Met, which clearly displayed that the modified electrode detects 10^{-3} M Cys at pH 1 and 2, whereas Met was sensed at pHs 1, 2 and 3. It was further confirmed by using DP Voltammetry, as shown in Figure 6b,d. These results support the cyclic voltammetric responses.
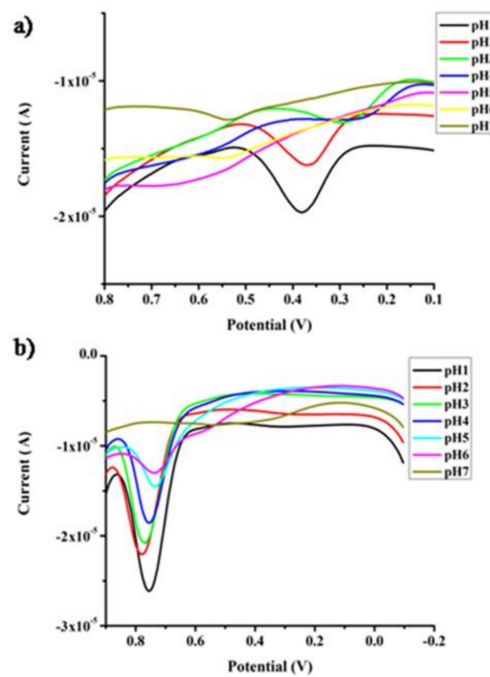
Figure 5. DP voltammogram of 10^{-2}M (**a**) Cys and (**b**) Met at CNOs–PS/Pt electrode in different pHs at a scan rate of 0.1 V/s.


Figure 6. Cyclic voltammogram of 3% CNOs–PS/Pt electrode for (**a**) Cys (10^{-3} M) and (**c**) Met (10^{-3} M) at different pHs; (**b**,**d**) are DP voltammograms of 10^{-3} M Cys and Met, respectively, at a scan rate of 0.1 V/s.

Plots of peak current against pH over the range of 1–7 are shown in Figure 7. It is clearly observed that the potential values for Cys and Met depend upon pH. As pH increases, the oxidation peak shift

towards more negative potential. The oxidation of Cys may lead to the formation of cystine, as shown in Scheme 1A,B and the ionization depends on pH [42,43]. The behavior of Met, as shown in Figure 7b, is similar to the previously reported pathway [43] in which the oxidation of Met may lead to the formation of methionine sulfone, as shown in Scheme 1C. At pH 1, the potential value of Met is low, as compared to pH 2, and any explanation for this behavior is difficult, but from pH 2, the potential values decreases.
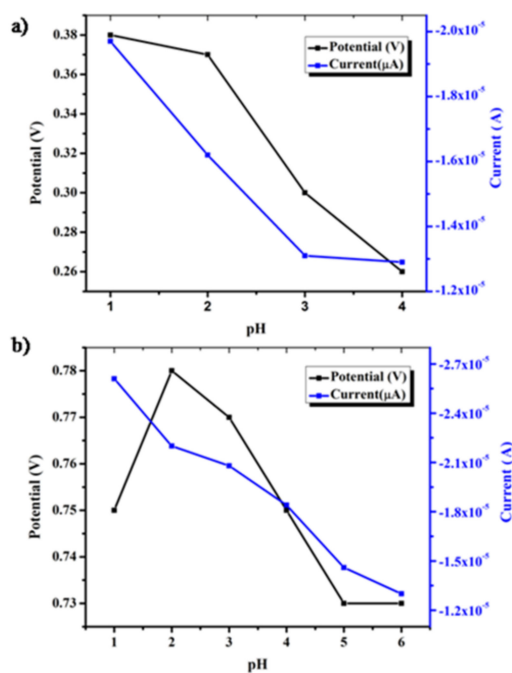

Figure 7. Effect of pH on the potential values and current height for (**a**) Cys and (**b**) Met. Scan rate: 50 mV/sec.
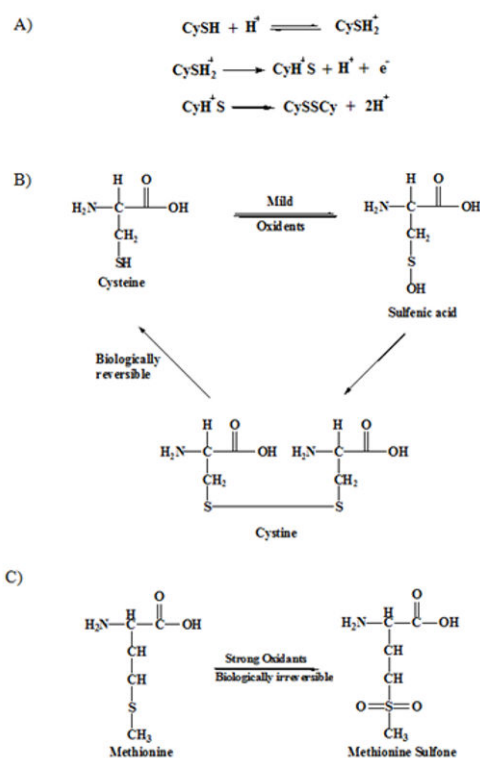
Scheme 1. Oxidations pathways for (**A,B**) Cys to cystine and(**C**) Met to methionine sulfone.

3.4. Determination of Cys and Met in a Mixture

To check the interference study, the modified CNO–PS/Pt electrode was applied directly to sense the mixture of Cys and Met (10^{-2} M each). We used a pH1 buffer to prepare the solution. The result is revealed in Figure 8, which clearly specifies that the CNO–PS/Pt electrode detects both the amino acids in the mixture. By using DP voltammetry, similar results were observed, as shown in Figure 7b.
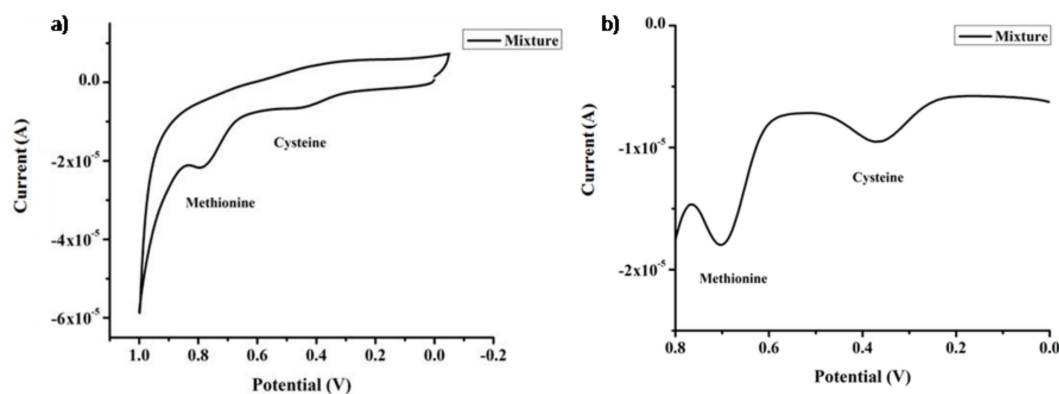
Figure 8. (**a**) Cyclic voltammogram of a mixture of Cys and Met (10^{-2} M) at CNOs–Ps/Pt electrode in 0.5 M KCl solution as supporting electrolyte and (**b**) DP voltammogram of the Cys and Met (10^{-2} M) at a scan rate of 0.1 V/s.

3.5. Detection of Cys in Green Beans

The newly modified electrode is used to detect Cys in a sample, such as green beans (*Phaseolus vulgaris*). Figure 9 shows the comparison of the detection of Cys by using the modified electrode and bare Pt electrode cyclic voltammetrically. The bare Pt electrode does not show any peak, whereas the modified electrode clearly shows a peak at +0.4 V, indicating the presence of Cys in green beans.
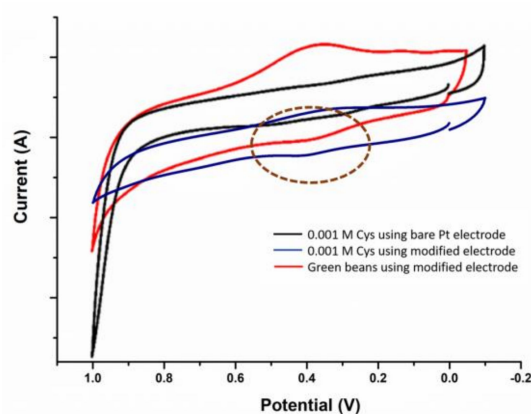
Figure 9. Cyclic voltammogram of extracted sample from green beans using bare Pt electrode and CNOs–Ps/Pt electrode.

We also calculated the total amount of Cys present in green beans from DP voltammetry. Comparing the current with the standard 0.01 M Cys sample, the amount of Cys in green beans was found to be 0.0097 g in 1 g green beans.

4. Conclusions

In conclusion, the successive detection of S-containing amino acids, Cys and Met, was carried out using a novel CNOs–PS composite-based modified Pt electrode. The detection of Cys and Met by

electrochemical methods is purely pH dependent and has a detection limit of 10^{-3} M. Moreover, the as prepared CNOs–Ps/Pt electrode qualitatively and quantitatively detects Cys in green beans. This is a comparatively simple, fast and precise method for detecting Cys and Met electrochemically.

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