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In situ monitoring of electrochemical reactions through CNT-assisted paper cell mass spectrometry†

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A novel method of coupling electrochemistry (EC) with mass spectrometry (MS) is illustrated with a paper-based electrochemical cell supported by carbon nanotubes (CNTs). The electrochemically formed ions, created at appropriate electrochemical potentials, are ejected into the gas phase from the modified paper, without the application of additional potential. The electrochemical cell was fabricated by using a rectangular CNT-coated Whatman 42 filter paper with printed electrodes, using silver paste. This was used for studying the electrochemical conversion of thiols to disulfides, and the functionalization of polycyclic aromatic hydrocarbons (PAHs), which involve S–S and C–C bond formations, respectively. We also demonstrate the versatility of the set-up by utilizing it for the detection of radical cations of metallocenes, monitoring the oxidation of sulfides through the detection of reactive intermediates, and the detection of radical cations of PAHs, all of which occur at specific applied potentials. Finally, the applicability of this technique for qualitative and quantitative analyses of environmentally relevant molecules has been demonstrated by studying the electrochemical oxidation of glucose (Glu) to gluconic acid (GlcA) and saccharic acid (SacA).

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Introduction

It has been more than four decades since researchers have been engaged in coupling electrochemistry with mass spectrometry (MS).[1–5] Being a sensitive analytical tool, mass spectrometry can be utilized for the identification of many molecular species revealing compositional and structural information. The importance of electrochemistry-mass spectrometry (EC-MS) resulted from two important facts. First, MS can act as an analytical tool to reveal structural and compositional information. Second, the coupling of EC with MS may enhance the ionization efficiency of many analytes which are difficult to be detected with mass spectrometry.[5,6] The coupling of EC with MS can lead to the identification of many electrochemical products[7] or reactants which are useful in bioanalytical applications.[8–18]

The first attempt to couple EC with MS was made in 1971 by Bruckenstein and Gadde.[1] They carried out an *in situ* mass spectrometric determination of volatile electrochemical reaction products. After that many developments have occurred in this field and several ionization methods have coupled EC with MS.[19–23] Thermospray (TS),[24] fast atom bombardment (FAB),[25] inductively coupled plasma (ICP),[26] chemical ionization (CI),[27] atmospheric pressure chemical ionization (APCI),[28] atmospheric pressure photoionization (APPI),[29] and electrospray ionization[30] are some of the techniques. Paper-based electrochemical cells offer many advantages over other types of cells because they are cheap, foldable, disposable, easy to use and simple.[31,32] The coupling of paper-based electrochemical cells with MS was first attempted recently by Liu *et al.*[33] They had employed the technique for studying various electrochemical cell reactions.

Paper spray, an ambient ionization technique, has been in use since 2010 and it has undergone tremendous changes over the past few years.[34] Normal paper spray ionization works in the high voltage range, but the incorporation of carbon nanotubes (CNTs) on the paper substrate made the analysis possible at 1 V.[35] This technique has been extended to other nanostructures.[36,37] In the present work, we have coupled a

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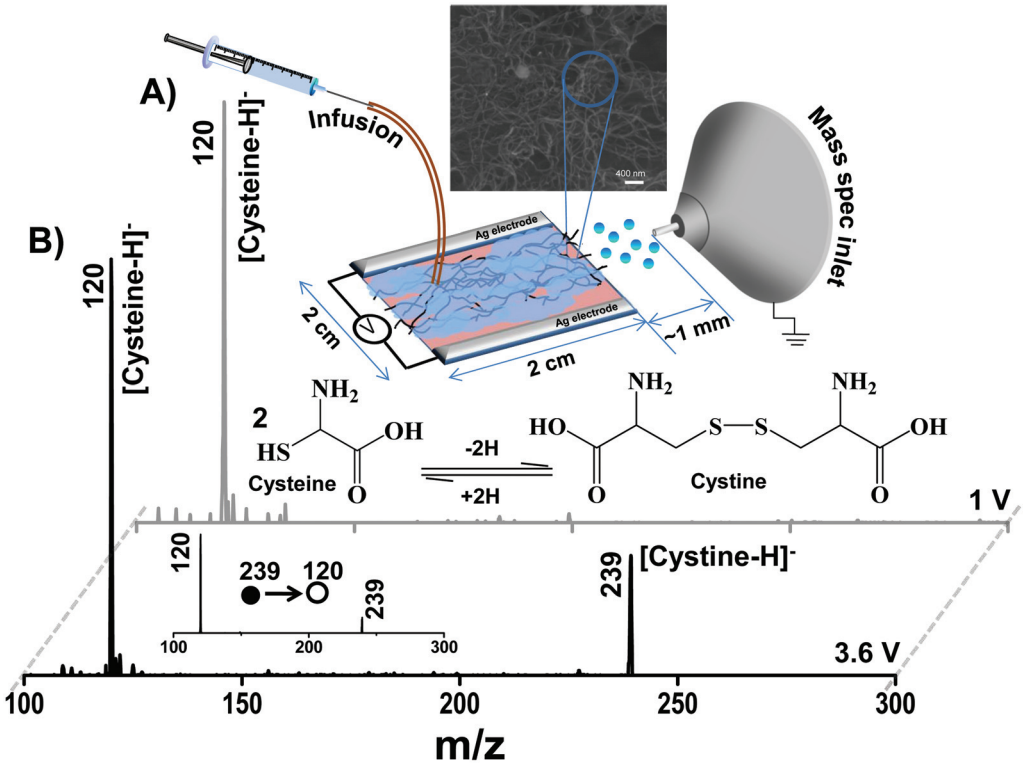

Fig. 1 (A) Normal low voltage (1 V) mass spectrum of cysteine collected from the CNT-coated paper. Schematic representations of the experimental set-up, along with an FESEM image of the CNT-coated paper, and the electrochemical oxidation of cysteine are shown in the inset. (B) Mass spectrum of cysteine collected from a paper-based electrochemical cell at a cell potential (ΔV) of 3.6 V. MS^2 data of the product ion peak is shown in the inset.

carbon nanotube coated paper-based electrochemical cell with MS and it has been utilized for the study of various electrochemical cell reactions; some applications have also been demonstrated. Compared to other reported EC-MS techniques, this technique allows the detection of electrochemically generated species at low voltages. Here the nanostructures have been used to achieve low voltage ionization and have helped in transporting electrochemically generated species from a paper-based cell to the mass spectrometer inlet. The present technique has been demonstrated for studying *in situ* S–S and C–C bond formation reactions as well as the electrochemical oxidation of analytes. We have understood the electrochemical oxidation of diphenyl sulfide through the detection of reactive intermediates. We have further demonstrated the generation of ions through an electrochemical oxidation event by coupling a CH electrochemical analyser with a mass spectrometer using a three electrode paper cell set-up.

Experimental

The paper-based electrochemical cells (both two and three electrode configurations) were fabricated from a modified carbon nanotube infused paper. A Whatman 42 filter paper in the required geometry was taken and metallic electrodes were patterned with silver paste for designing an electrochemical cell. CNTs were obtained from Nanocyl SA, USA. The sample was composed of 1 μm long multiwalled CNTs of mixed diameters. A CNT suspension was prepared in water and was coated in the space between the two electrodes, leaving a gap of nearly 2 mm near the electrodes in order to avoid the possibility of short circuit (Fig. 1A). This set-up was used in most of the studies. More detailed studies were performed with the three electrode set-up.

The two electrode cell was connected with an external voltage supply and was held in front of the mass spectrometer inlet. All mass spectrometric measurements were done using a linear ion trap LTQ XL of Thermo Scientific, San Jose, California. Mass spectrometric conditions used are presented in the ESI.† All analytes used were at ppm concentrations and they were infused using a syringe pump for each measurement. The following conditions were the experimental conditions for mass spectrometry: source voltage: 0 V and above, capillary temperature: 150 °C; capillary voltage: 0 V; and tube lens voltage: 0 V. The collision-induced dissociation technique was used for MS^2 analysis. A field emission scanning electron microscope (FESEM) was used for imaging the modified paper. Methanol, dichloromethane (DCM), acetonitrile (ACN) and sulphuric acid were purchased from Rankem. Trifluoroacetic acid, KCl, ferrocene, ferrocenecarboxaldehyde, nickelocene, glucose, diphenyl sulfide (PhSPh), 1,2-benzanthracene, and naphthalene were bought from Sigma Aldrich,

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India. Sodium acetate and acetic acid were purchased from Merck Ltd, Mumbai, India. Cysteine (Cys) was bought from Fisher Scientific Pvt. Ltd, Mumbai, India, and glutathione was from Sisco Research Laboratories Pvt. Ltd, Mumbai, India. Benzene was bought from S D Fine Chem Ltd, Chennai, India. Mesitylene was bought from Spectrochem Pvt. Ltd, Mumbai, India. The blood serum sample used in this work was obtained from the collection that was part of a recent study.[38] The sample belonged to a non-diabetic control participant. Ethical clearance was obtained from Kovai Medical Centre and Hospital, Coimbatore, India (Ref. EC/AP/356/02/2015 dated 16/02/2015), with informed consent from the participant.

In a similar way, the three electrode set-up was prepared in which the length of the middle electrode was made smaller than the other two to avoid hindrance during paper spray ionization. Detailed *in situ* electrochemical analysis and mass spectrometry were carried out by placing this three electrode paper cell in front of a mass spectrometer inlet and the three electrodes of the paper cell were connected to a CH 600A electrochemical analyser. Cyclic voltammetry was performed to obtain the oxidation potential of the analytes. The electrodes were connected in such a manner that the middle electrode was the reference and the other two were the working and counter electrodes, respectively. To demonstrate the methodology of ion generation through the electrochemical event, ferrocenecarboxaldehyde was chosen as a potent candidate. Paper used for the construction of the cell was the same as that used before.

Results and discussion

A paper-based two electrode electrochemical cell (Fig. 1A) was placed in front of the MS inlet at a distance of 1 mm from it and was connected to an external voltage supply. A DC voltage was applied across the cell through the Ag electrodes. Analytes, along with the solvent and the electrolyte, were introduced on the cell with the help of a continuous sampling system (syringe injection pump). Data from the three electrode set-up will be presented at a later part of the paper.

Monitoring electrochemical reactions

One of the major advantages that comes with coupling electrochemistry with low voltage paper spray ionization mass spectrometry is the capability to *in situ* monitor the electrochemical reactions. Here we have demonstrated reactions that involve S–S and C–C bond formations. In addition to this we have also demonstrated the oxidation of analytes such as metallocenes, PAHs, and glucose.

Electrochemical S–S bond formation reaction

Oxidation of cysteine to cystine. Initial measurements were carried out with a well-known electrochemical reaction which is the conversion of thiols to disulfides *via* electrochemical oxidation. For this, cysteine was chosen and its solution was prepared in a methanol : water (1 : 1 by volume) mixture at 100 ppm concentration. About 100 ppm of KCl (in water) was used as the electrolyte. Following the introduction of the sample solution on the cell, the potential was varied across the cell with the help of an external power supply. The results are shown in Fig. 1.

Fig. 1A shows a typical low voltage mass spectrum of cysteine at 1 V showing a deprotonated molecular ion peak at m/z 120. This was collected from the CNT-coated paper containing cysteine in methanol : water (1 : 1 by volume), by the application of 1 V on it. Other mass spectrometric conditions are presented in the ESI.† A solution of KCl at 100 ppm concentration (electrolyte) was applied on the paper-based cell followed by the introduction of cysteine in methanol : water (1 : 1 by volume), with an injection syringe. A cell potential (ΔV) of 3.6 V was applied across the electrodes and the resulting mass spectrum is shown in Fig. 1B. Here a deprotonated peak of cysteine disulfide appears at m/z 239 along with the peak at m/z 120. MS^2 analysis confirmed the identity of the product ion (inset of Fig. 1B). Here a typical electrochemical strategy is followed for the formation of disulfide from cysteine; the reaction scheme is shown in the inset of Fig. 1A. It occurs through an electrochemical oxidation, involving the removal of two hydrogens from two molecules of cysteine, leading to the formation of cysteine disulfide by S–S linkage. It is clear from the control experiment that the reaction requires an electrochemical environment. The expected product (cystine disulfide), was not observed neither during the typical low voltage paper spray ionization experiment nor from a paper cell, at cell potential of 0 and 1 V (Fig. S2A, ESI†). The mechanism of formation of the electrochemical products from the current experiment involves two important events. First is the electrochemical oxidation of the analyte species on the paper by the application of voltage and second is the low voltage ionization of the formed species from the paper with the aid of CNTs protruding from the paper.[35] These two events together make the reaction possible at 3.6 V.

The electrochemical mechanism was tested by a voltage variation study, in which the same experiment was carried out by sweeping the voltage from 0 V to 6 V. It was observed that the electrochemically formed cysteine disulfide peak appeared at 3.6 V and reached a saturation value at 4 V. Fig. S1A (ESI†) shows the product ion intensity (cysteine disulfide) as a function of applied voltage, suggesting the involvement of electrodic event in the reaction pathway. The mass spectra collected at different voltages in the voltage variation experiment are shown in Fig. S2A (ESI†).

Oxidation of glutathione. A replication of the same experiment with glutathione resulted in glutathione disulfide in a similar manner (Fig. 2). A solution of glutathione was prepared in a methanol : water solvent system (1 : 1 by volume). The experiment was performed in a way similar to cysteine. The cell potential was varied from 0 to 6 V. The electrochemically formed glutathione disulfide was detected at 3.6 V. A further increase in the voltage resulted in the saturation of the product ion intensity at 4 V (Fig. S1B, ESI†). Fig. 2A shows the 1 V mass spectrum and Fig. 2B shows the spectrum at a cell potential of 3.6 V. The latter shows the presence of an electro-

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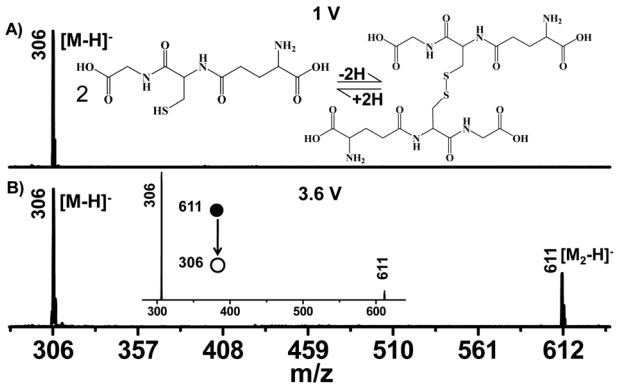

Fig. 2 (A) Normal low voltage (1 V) mass spectrum of glutathione collected from the CNT-coated paper, and (B) mass spectrum of glutathione at a cell potential (ΔV) of 3.6 V. MS^2 spectrum of glutathione disulfide is shown in the inset of B. Schematic representation of the electrochemical oxidation of glutathione is shown in the inset of A.

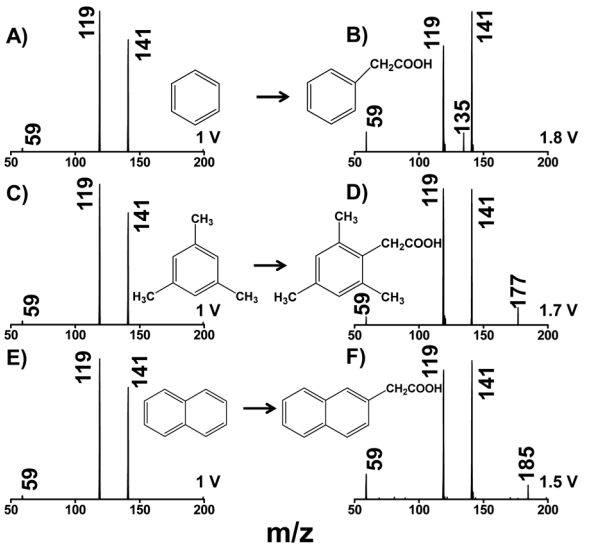

Fig. 3 Electrochemical functionalization of different hydrocarbons. Low voltage mass spectra of (A) benzene, (C) mesitylene, and (E) naphthalene, respectively, in acetic acid containing sodium acetate, at 1 V (blank experiments). Mass spectrum showing the electrochemical functionalization of (B) benzene to benzene acetic acid at a cell potential (ΔV) of 1.8 V, (D) mesitylene to mesitylene acetic acid at a cell potential (ΔV) of 1.7 V, and (F) naphthalene to naphthalene acetic acid at 1.5 V across the electrode. The spectra were collected in negative ion mode. Schematic representations of these three reactions are also shown.

chemically formed glutathione disulfide. The MS^2 spectrum shown in the inset of Fig. 2B confirms the product.

The results obtained during a voltage variation experiment are shown in Fig. S2B (ESI†). Fig. S2B (ESI†) shows the mass spectra collected for the voltage variation study. These two results support an electrodic event involved in the observed species.

Electrochemical C–C bond formation reactions. To demonstrate the monitoring of electrochemical C–C bond formation reactions, three hydrocarbons, *viz* benzene, mesitylene, and naphthalene, were selected as reagents. This also indicates the additional advantage that comes by coupling EC with low voltage MS wherein such undetectable species (typically, molecular species without any functional groups) are detected *via* electrochemical functionalization. The solutions of these analytes were prepared in a 1 : 1 acetic acid : sodium acetate mixture at 100 ppm concentration. Here acetic acid acted as a solvent and sodium acetate as an electrolyte as well as a reagent. The mixture was continuously injected into the electrochemical cell and the potential was swept from 0 to 5 V. The results are shown in Fig. 3

Fig. 3A shows a control experiment carried out with benzene in acetic acid and sodium acetate. This mass spectrum was collected using the normal low voltage paper spray ionization technique. The spectrum shows the presence of an acetate ion, a proton bound dimer of the acetate ion and a sodium bound dimer of the acetate ion at *m*/*z* 59, 119 and 141, respectively. No benzene was detected. The same set of analytes were introduced on the paper-based electrochemical cell and the DC voltage was changed from 0 V to higher positive voltages. As a result, a new product peak appeared at *m*/*z* 135 at a cell potential of 1.8 V (Fig. 3B) and it has been assigned as benzene acetic acid as confirmed from MS^2 data shown in Fig. S3A (ESI†). Similar experiments were performed with mesitylene and naphthalene as well (Fig. 3C–F). Note that parent hydrocarbons were not detected. Two new peaks appeared at *m*/*z* 177 and 185 (Fig. 3D and F) corresponding to the carboxylated products of mesitylene and naphthalene, respectively (mesitylene acetic acid and naphthalene acetic acid). The corresponding MS^2 data are shown in Fig. S3B and S3C (ESI†). A voltage variation study was performed with these analytes in order to prove the event as an electrodic event. For this, each of these analytes were introduced on the electrochemical cell and the external power supply was swept from 0 V to higher voltages. The results are shown in Fig. S4 (ESI†). In the case of benzene, a new peak corresponding to benzene acetic acid started to appear at 1.8 V and got saturated at 2 V.

For mesitylene, the carboxylated peak appeared at 1.7 V and got saturated at 1.9 V. Similarly for naphthalene, the peak appeared at 1.5 V and got saturated at 1.7 V. These experiments proved that the above events occurred as a result of an electrochemical pathway occurring at the electrode. The mass spectra collected in a voltage variation study are shown in Fig. S5 (ESI†). We did not see the presence of multiply carboxylated hydrocarbons as a result of electrochemical functionalization, the reason for which is unclear at present.

Electrochemical oxidation of metallocenes. Metallocenes are another class of compounds which can be oxidized electrochemically. Here we have used the paper-based electrochemical cell in order to ionize selected metallocenes *via* electrochemical oxidation. For this, three metallocenes were chosen and solutions were prepared in a ACN/CH_2Cl_2 solvent mixture (1 : 1 by volume) at 100 ppm concentration. The cell was saturated with trifluoroacetic acid as an electrolyte and the analytes were applied with the help of an injection syringe.

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Subsequently the potential was applied through an external power supply. The results are shown in Fig. 4.

The results show the presence of metallocenes as radical ions generated *via* electrochemical oxidation. The insets of Fig. 4A–C show the mass spectra of metallocenes (in ACN/CH_2Cl_2 with trifluoroacetic acid as an electrolyte), collected from the paper cell at a cell potential of 0 V. These blank spectra suggest the absence of an electrochemical event when the cell is in off condition. The electrochemically generated radical ions appeared at the corresponding cell potentials when the voltage was swept from 0 V to higher voltages. These results are shown in Fig. 4A–C for ferrocene, ferrocenecarboxaldehyde, and nickelocene, respectively. These results provide evidence for an electrodic event.

Monitoring oxidation reaction of diphenyl sulfide. Anodic oxidation of diphenyl sulfide is a well-known electrochemical reaction whose mechanism proceeds *via* an unstable radical cation.[33] This cation has been detected. For this, diphenyl sulfide was introduced on the cell in the ACN/CH_2Cl_2 solvent system along with KCl as an electrolyte at 100 ppm concentration. The potential was applied with the help of an external power supply and the mass spectrum was recorded. The actual mechanism of diphenyl sulfide oxidation proceeds *via* the formation of an unstable radical cation, finally leading to the formation of a pseudo dimer sulfonium ion followed by hydration. Scheme 1 shows the mechanism involved in the oxidation of diphenyl sulfide.

The mass spectrum collected at a cell potential of 1.2 V in Fig. 5 shows the presence of the unstable radical cation at *m*/*z* 186.

This cation loses a proton and forms a deprotonated species of mass 185. The other species that were detected included a pseudodimersulfonium ion and its hydrated adduct, at *m*/*z* 371 and 387, respectively. A plot of the product ion intensity *vs.* voltage (Fig. S6, ESI†) shows the emergence of an electrochemically activated species (product ions and reaction intermediates) at a cell potential of 1.2 V followed by saturation at 1.8 V.

Quantification of glucose in body fluid. The cell has been used for the identification of some environmentally relevant species in both a quantitative and qualitative manner. Electrochemical oxidation of Glu to GlcA and SacA is a well-studied electrodic event of biological relevance. As a trial method, Glu solution was prepared in Millipore water at a con-

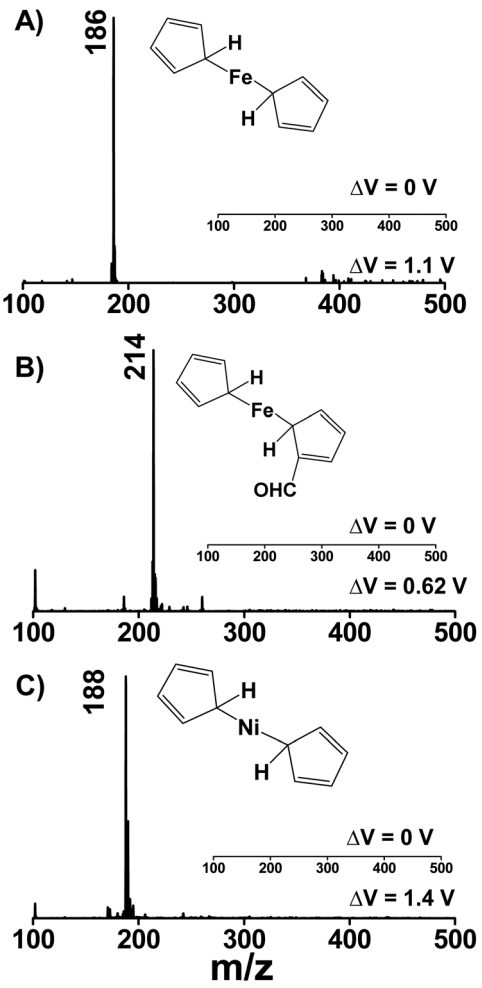
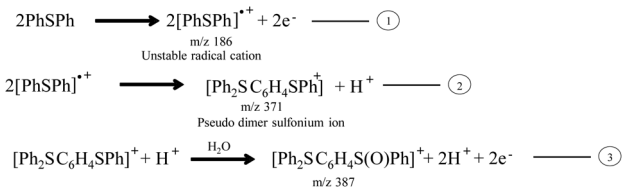


Fig. 4 Electrochemical oxidation of metallocenes. Mass spectra of (A) ferrocene, (B) ferrocenecarboxaldehyde, and (C) nickelocene at cell potentials (ΔV) as indicated in the inset in each case, collected in positive ion mode. For all cases, ACN/CH_2Cl_2 was used as the solvent mixture with trifluoroacetic acid as an electrolyte. The corresponding mass spectra obtained at a cell potential (ΔV) of 0 V, is shown in the inset in each case. Peaks, other than those labelled, are due to the background.



Scheme 1 Schematic representation of the possible mechanism of diphenyl sulfide oxidation.[33]

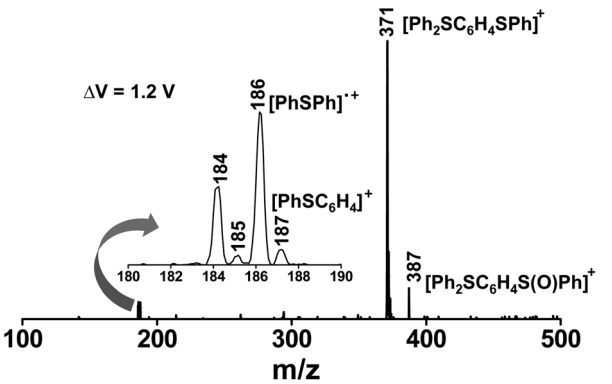


Fig. 5 Mass spectrum of diphenyl sulfide (in ACN/CH_2Cl_2 solvent mixture with KCl as an electrolyte) collected from the paper cell at a cell potential (ΔV) of 1.2 V. The spectrum is in the positive ion mode.

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centration of 100 ppm and it was applied on the cell along with a small amount of H_2SO_4 (1%). The application of a DC voltage of 3.4 V across the cell resulted in the oxidation of Glu to both GlcA and SacA. The inset of Fig. 6A shows a normal low voltage (1 V) mass spectrum of Glu (in Millipore water containing 1% H_2SO_4), which clearly shows the presence of a deprotonated peak of glucose at *m*/*z* 179. The same set of reagents were applied to the paper cell and it showed the presence of both GlcA and SacA formed as a result of Glu oxidation at a cell potential of 3.4 V (Fig. 6A). A voltage variation study confirmed the oxidation as an electrodic event and the result is shown in Fig. 6C.

This experimental result prompted us to carry out qualitative and quantitative analyses of blood serum glucose. For this, the paper cell was saturated with blood serum along with a small amount of H_2SO_4 and the cell potential was varied and it resulted in the formation of GlcA and SacA at 3.4 V (Fig. 6B). A quantitative analysis was carried out with a series of concentrations of glucose and the results are shown in Fig. 6D and S7 (ESI†). These results clearly show a glucose concentration of 0.45 μM in the blood serum. The value is in good agreement with the expected value of glucose in blood for a normal person.[39]

Selective detection of polycyclic hydrocarbons. We demonstrate the practicality of the paper-based electrochemical cell for a selective detection of hydrocarbons from a mixture (Fig. 7). For this, three hydrocarbons were chosen and their mixture (in ACN/CH_2Cl_2) was saturated on the cell along with KCl as the electrolyte. The mixture was applied in two different ways on the cell, in equimolar and non-equimolar concentration ratios. A variation of voltage from 0 V to higher voltages resulted in the emergence of each hydrocarbon according to its oxidation potential. Fig. 7 presents the result which shows the presence of 1,2-benzanthracene, naphthalene, and benzene at cell potentials of 1.2 V, 1.5 V and 1.8 V, respectively. Variations in ion intensities for each of the ions depend on multiple factors such as ionization efficiency, stability of the ions in solution, efficiency of ion transport into the MS, *etc*. The capability of the cell to identify environmentally relevant species has been demonstrated through the detection of 1,2-benzanthracene and glucose. The detection limits of the species were 1 ppt and 10 ppm for glucose and 1,2-benzanthracene, respectively (see Fig. S8, ESI†).

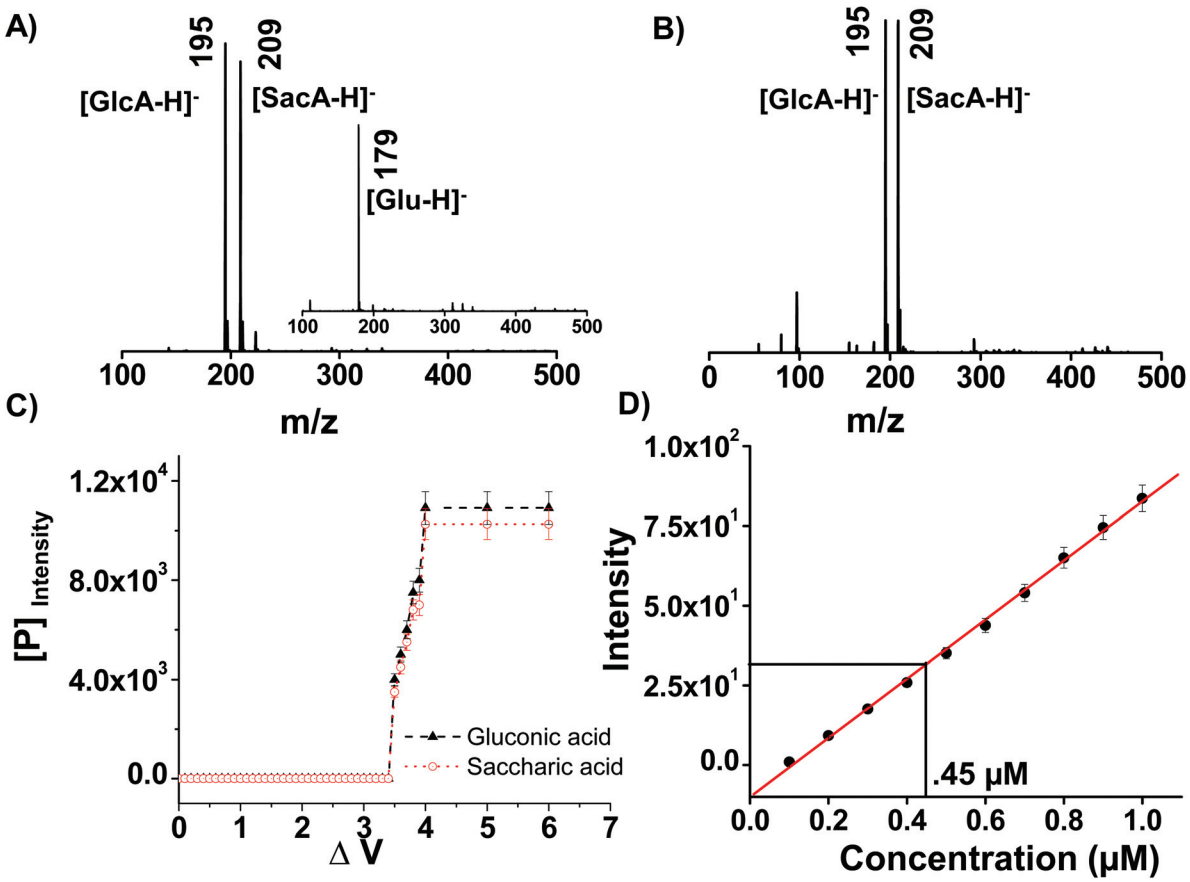

Fig. 6 Electrochemical oxidation of Glu. (A) Mass spectrum of glucose collected from a paper-based electrochemical cell at a cell potential (ΔV) of 3.4 V. Normal low voltage (1 V) mass spectrum of glucose collected from the CNT-coated paper is shown in the inset. (B) Mass spectrum of the human blood serum collected from a paper-based electrochemical cell at a cell potential (ΔV) of 3.4 V, showing the presence of Glu in it. Peaks, other than those labelled, are due to the background. (C) A plot of product ion intensity (electrochemically generated species) as a function of applied voltage for glucose detection. (D) Intensity–concentration profile for Glu to GlcA oxidation.

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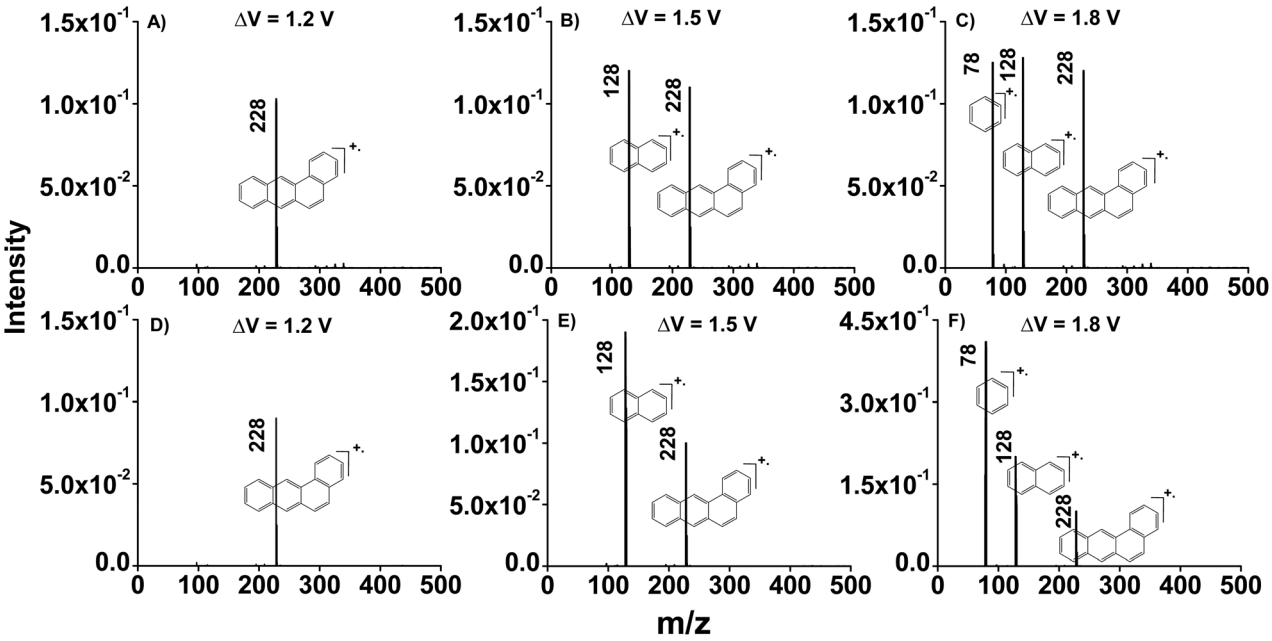

Fig. 7 Electrochemical oxidation of a mixture containing different hydrocarbons at different cell potentials. A, B, and C show mass spectra of an equimolar mixture of benzene, naphthalene and 1,2-benzanthracene, showing the presence of electrochemically oxidized hydrocarbons at their respective cell potentials with equal ion intensities. D, E, and F show mass spectra of a non-equimolar mixture of benzene, naphthalene and 1,2-benzanthracene showing the presence of electrochemically oxidized hydrocarbons at their respective cell potentials with different ion intensities.

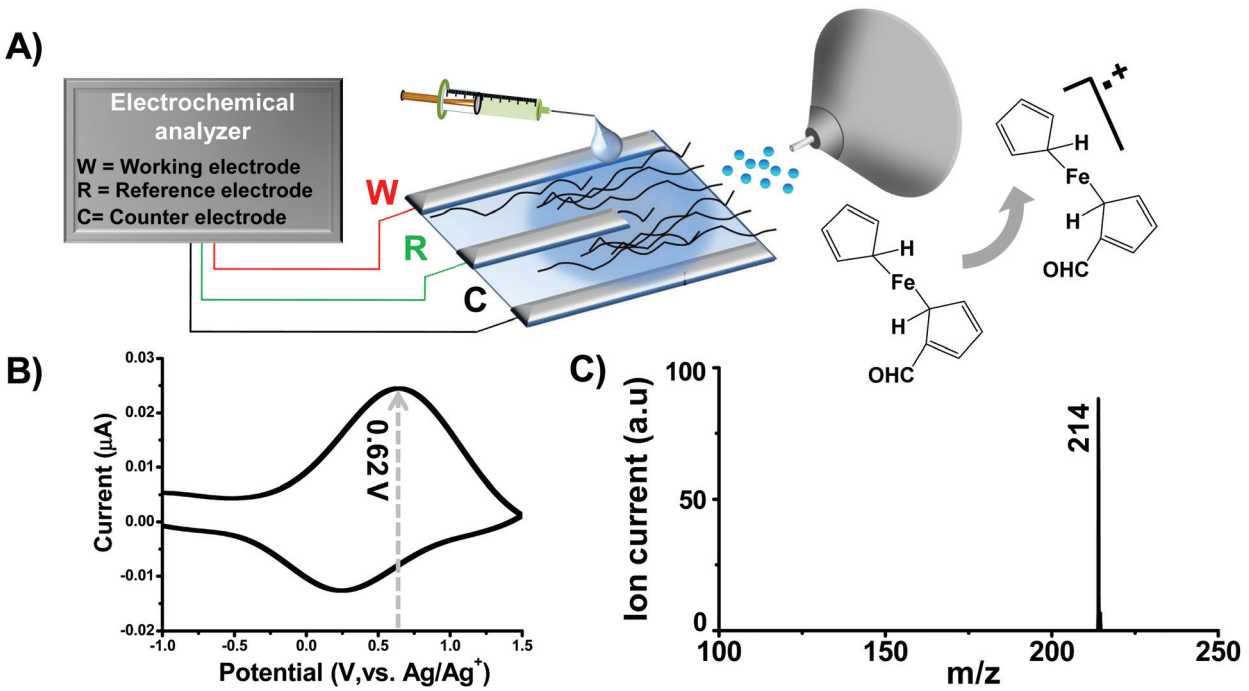

Fig. 8 *In situ* analysis of the electrochemical oxidation of ferrocenecarboxaldehyde with three electrode paper cell mass spectrometry coupled with an electrochemical analyzer. (A) Schematic representation of the coupled set-up. (B) Cyclic voltammogram and (c) *in situ* mass spectrum of the electrochemically oxidized species of ferrocenecarboxaldehyde.

***In situ* monitoring of ferrocenecarboxaldehyde and PAH oxidation reaction.** Fig. 8 shows a schematic representation of the experimental set-up, in which a three electrode based electrochemical cell was designed on a CNT coated Whatman 42 filter paper, coupled with a CH electrochemical analyser and a mass spectrometer. This experiment was performed to

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confirm whether the phenomena outlined above occur under standard electrochemical conditions. Fig. 8B shows the cyclic voltammogram of the redox reaction. The characteristic oxidation peak of ferrocenecarboxaldehyde is seen at ~0.62 V (*vs.* Ag/Ag^+ electrode). The data are in good agreement with the previous report in which CV was measured in the standard three electrode system where gold electrodes were used.[40] At the same time, we monitored the mass spectrum of the oxidised species of ferrocenecarboxaldehyde in positive ion mode, shown in Fig. 8C. The peak at *m*/*z* 214 corresponds to the ferrocenecarboxaldehyde ion which supports the electrochemical oxidation phenomenon. For polycyclic aromatic hydrocarbons, the required potentials (threshold potentials) to eject the electrochemically oxidised species to the gas phase for mass spectrometric analysis are slightly different from the oxidation potentials in the solution phase. However, we observed that these threshold potentials follow a similar trend, similar to the oxidation potentials. In Table S1 (ESI†), the oxidation potentials and the potentials required for mass spectrometric detection in a three electrode paper cell of benzene, naphthalene, and 1,2-benzanthracene are listed. These oxidation potentials are in good agreement with the literature.[41] Fig. S9 (ESI†) presents the cyclic voltammogram of benzene, naphthalene, and 1,2-benzanthracene.

Conclusions

In conclusion, we report a CNT incorporated paper-based electrochemical cell which utilizes the advantages of both low voltage ionization and electrochemistry. Integrating these two principles makes the *in situ* ionization and detection of analytes at low voltage possible, by electrochemically transforming them. Using this device, we have studied the electrochemical conversion of thiols to disulfides. The electrochemical functionalization of three different hydrocarbons has been performed with the paper-based electrochemical cell. Additionally, the detection of metallocenes as well as an unstable radical cation has been achieved with the cell. The study shows that a detection limit of 1 ppt can be reached for specific species. Quantitative analysis is also possible as demonstrated in the case of glucose. The cell has been used for the analysis of different environmentally relevant species. These results open up the possibility of developing such point-of-use devices for various applications by combining known techniques, using nanomaterials.

Conflicts of interest

There are no conflicts to declare.

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