CHAPTER 6

In-situ Electrochemical Transformation of Aminobenzene Sulfonic Acid Isomers to Respective Surface-Confined Redox Active Quinones by Passing Polyaniline on MWCNT Surface for NADH Sensing

6.1 Introduction

Sulfanilic acid (SA) or aminobenzene sulfonic acid, a derivative of aniline, has been widely used as a precursor for the preparation of self-doped conductive sulfonated polyanilines (SPAN) (Freund and Deore, 2007; Yue and Epstein, 1990). Owing to the unique electrochemical and physical properties like water solubility (due to its ionic structure), enhanced conductivity, thermal stability and optimal activity, SPAN has been utilized for various applications such as, rechargeable batteries (Barbero et al., 1994), junction devices (Narasimhan et al., 1998) anticorrosive coatings (Ionit and Prun, 2011), ultra-filtration membranes (McVerry et al., 2013) and electro-catalysis (Xi et al., 2016; Jin et al., 2005; Kumar and Chen, 2007a). Previously, ortho, meta and para-isomers of SA have been successfully electro-polymerized as poly aminobenzene sulfonic acids (PABS) on GCE (Xi et al., 2016; Jin et al., 2005; Kumar and Chen, 2007a; 2007b), Pt (Sahin et al., 2003), Au (Pillay and Ozoemena, 2009; Agboola et al., 2010) and ITO (Shieh et al., 2010). To the best of our knowledge, electrochemical reaction of SA to non-polymeric substances has never been reported. Herein, we reveal a unique and selective electrochemical transformation of ortho- (o-SA), meta-(m-SA) and para-aminobenzene sulfonic acid (p-SA) to surface-confined redox active quinone (catechol, CA; resorcinol, Re; hydroquinone, HQ), without any conducting polymer like product formation one observed with conventional SA systems, on multi walled carbon nanotube (MWCNT) modified GCE surface (GCE/MWCNT@HQ, HQ = hydroquinone).

In general, acid or alkaline salt solution and wider potential window (-1.2 — 0.8 V vs Ag/AgCl) based condition has been used for the electro-polymerization of SA and
its derivatives (Xi et al., 2016; Jin et al., 2005; Kumar and Chen, 2007a; 2007b; Wanekaya et al., 2006; Branzoi, 2009; Liu et al, 2005). Such procedure often resulted to formation of capacitive like electrochemical system with a feeble redox peak at an equilibrium potential ($E_{1/2}$) ~ 0 V vs Ag/AgCl in alkaline salt and neutral pH conditions. For instance, a redox peak at $E_{1/2} =$ (i) 0.5 V vs Ag/AgCl with p- (PABS) modified GCE/MWCNT in 0.1 M KCl (Xi et al., 2016), (ii) 0.15 V vs Ag/AgCl with m-PABS/SWCNT (SWCNT-single walled carbon nanotube) in pH 7.4 phosphate buffer solution (PBS) (Pillay and Ozoemena, 2009; Agboola et al, 2010), (iii) -0.1 V vs Ag/AgCl with PPy/m-PABS/SWCNT (PPY-polypyrrole) in 0.5 M NaCl (Wanekaya et al., 2006), (iv) 0.2 V vs Ag/AgCl with PPy/PABS/SWCNT in 0.25 M KCl (Branzoi, 2009) and (V) 0 V vs Ag/AgCl with PANI/PABS-SWCNT in pH 7.2 PBS (Liu et al, 2005) were reported. The above redox peak systems have been referred as an electrochemical behaviour of the polyaniline derivatives. On contradictory, in this work, we revealed that the p-SA’s redox peak observed at 0 V vs Ag/AgCl is a surface-confined quinone redox system (i.e., GCE/MWCNT@HQ), not as a polyaniline redox transitions. It is interesting to highlight that at restricted potential window, -0.4 to 0.4 V vs Ag/AgCl and pH 7 PBS, SA isomers get electro-oxidized as quinone derivatives on CNT surface. Experiments at other conditions such as wider working potential window, i.e., over to -0.4 – 0.4 V vs Ag/AgCl and non pH 7 PBS solution resulted to formation of thick PANI film with feeble redox peak at 0 V vs Ag/AgCl, as like the observation noticed with the conventional PABS systems (Xi et al., 2016; Jin et al., 2005; Kumar and Chen, 2007a; 2007b).

Quinone immobilized carbon-chemically modified electrodes have been widely used for various technical applications. For example, energy storage batteries (Jaffe et al., 2015), super-capacitors (Pignon et al., 2012), biofuel cells (Giroud et al., 2015), and electro-catalysis (Swetha et al., 2014). In general, for the preparation of quinone chemically modified electrodes, covalent attachment via carbon-carbon (Kumar et al., 2010), carbon-nitrogen (Kanazawa et al., 2010) and Michael addition reaction (Dey et al., 2010), self-assembled monolayer (Behera et al., 2008) and adsorption through pyrene derivatives (Giroud et al., 2015) routes have been adopted. Except a few, most of the quinone modified electrodes show poor stability and weak redox feature in aqueous
solution (Kumar et al., 2010). New quinone immobilized MWCNT modified GCEs prepared in this work by in-situ SA electro-oxidation method via desulfonation and deamination reactions showed stable and efficient redox active system suitable for electrochemical and electro-analytical applications. A strong π-π interaction and its restricted diffusion of SA on MWCNT make the system so facile for the unique electrochemical transformation reaction. Selective and low potential (0.15 V) electro-catalytic oxidation and sensing of reduced form of nicotinamide adenine dinucleotide (NADH) using GCE/MWCNT@HQ was demonstrated as a model system.

6.2 Experimental Section

6.2.1 Reagents and Materials

MWCNTs (>90% carbon basis, outer diameter, 10-15 nm; inner diameter, 2-6 nm; length, 0.1-10 μm), ortho and meta-aminobenzene sulfonic acids (>99% purity) were obtained from Sigma Aldrich. Para-aminobenzene sulfonic acid (>99% purity) was purchased from Fluka, India. Other chemicals used were of analytical grade and used as received without any further purification. Aqueous solutions were prepared using deionised and alkaline KMnO₄ double distilled water. The supporting electrolyte, pH 7 phosphate buffer solution (PBS) of ionic strength, I = 0.1 mol L⁻¹, was used throughout this work.

6.2.2 Instrumentation

Voltammetric measurements were carried out using Metrohm Autolab, Netherlands. The three-electrode system consisted of a GCE (Bioanalytical System, USA; 3 mm diameter, 0.0707 cm² area) or of its chemically modified electrode, as a working electrode, Ag/AgCl as a reference electrode, and a platinum wire as an auxiliary electrode. In-situ CV-EQCM experiments were carried out using a gold single crystal electrode (EQCM-Au) of geometric surface area = 0.19 cm² with a CHI 440 B workstation (USA). For the physico-chemical characterizations, transmission electron microscope (FEI TECNAI 20, Netherland), FTIR (JASCO 4100, Japan), Raman
spectrophometer (AZILTRON, PRO 532, USA) with a 532 nm laser excitation source and GC-MS (A Jeol GCMATE II instrument, Japan) instruments were used. Purified-MWCNT sample was prepared by acid treatment method as per our previous reported procedure (Vishnu and Kumar, 2016). Using continuum source electro-thermal atomic absorption spectrometry (CS-ETAAS) technique, iron impurity in carbon samples was quantified as: MWCNT-2.1 wt.%; p-MWCNT-0.6 wt.%; carbon nanofibre-0 wt.%; graphite nanopowder-0.22 wt.% (Vishnu and Kumar, 2016).

**Scheme 6.1** Cartoon for the Electrochemical Polymerization of p-SA to Sulfonated Polyaniline (SPAN) (A and B) and Transformation of p-SA to Hydroquinone (C and D) on Iron Impurity Containing MWCNT Modified Glassy Carbon Electrode System by Potential Cycling Experiment Following Set-I or Set-II Conditions Respectively. Followings are Control Experiments Relating to Electrochemical Oxidation/Reduction Reaction of p-SA at the Set-I Condition in pH 7 PBS with; N$_2$ Purged (E), Purified-MWCNT Modified Electrode in Dissolved Oxygen (F) and With N$_2$ Purged Solution and Deliberated added H$_2$O$_2$ (500 µM) (G) Conditions.
6.2.3 Procedure

Prior to the modification, surface of the GCE was cleaned both mechanically (polished with one micron alumina powder in the bio-analytical system polishing kit, cleaned with acetone, followed by distilled water) and electrochemically (by performing CV for 10 cycles in the potential window from -0.2 to 1.0 V vs Ag/AgCl in pH 7 PBS at scan rate (v) = 50 mVs\(^{-1}\)). In first, MWCNT modified GCE (GCE/MWCNT) was prepared by drop-casting 10μL of MWCNT-ethanolic suspension (2 mg in 500 μL) on a pre-treated GCE and air dried for 5±1 min. In a similar way, other carbon material modified GCE surfaces were also prepared. Electrochemical transformation of SA to quinone was performed by twenty continuous potential cycling of GCE/MWCNT with 15 mM of respective SA isomer dissolved in pH 7 PBS at a potential window of -0.4 to 0.4 V vs Ag/AgCl at scanrate (v) of 50 mV s\(^{-1}\) (Scheme 6.1 A-D). Such electrochemical procedure resulted to stable surface confined redox-active quinone species (GCE/MWCNT@Q) in pH 7 PBS. Freshly prepared GCE/MWCNT@Quinones were pre-treated at the same potential window for ten continuous potential cycles in pH 7 PBS at scan rate = 50 mV s\(^{-1}\). For the physicochemical characterizations such as FT-IR and Raman, a screen printed carbon electrode (SPCE) was used as a working electrode.

6.3 Results and Discussion

6.3.1 Electrochemical Oxidation of SA on GCE/MWCNT Modified Electrode

Initial electrochemical oxidation experiment was carried out with p-SA and unmodified GCE in a short potential window (set-I), -0.4 to + 0.4 V vs Ag/AgCl at a scan rate 50 mV s\(^{-1}\). As can be seen in Fig. 6.1 A, curve a, featureless voltammetric response was observed indicating electro-inactivity of the GCE for p-SA in a neutral pH condition. Interestingly, when the same experiment was repeated with pristine-MWCNT modified GCE (GCE/MWCNT), a sharp and constantly growing redox peak at equilibrium potential, \(E_{1/2}\) (\(E_{1/2} = E_{pa}+E_{pc}/2\); where \(E_{pa}\) and \(E_{pc}\) corresponding to the anodic and cathodic peak potentials) and peak-to-peak separation (\(\Delta E_p = E_{pa}-E_{pc}\)) of 80.5±5 mV vs Ag/AgCl and 15±3 mV vs Ag/AgCl were observed (Fig. 6.1 A, curve b). After twenty
continuous CV cycles, the working electrode was gently washed with distilled water then transferred to a blank pH 7 PBS and CV was performed again. As can be seen in Fig. 6.1 B, curve a, the same redox peak was retained without any alteration in the peak potential along with a relative standard deviation (RSD) = 0.1% and surface excess ($\Gamma$) = 1.1 n mol cm$^{-2}$.

![Graph](image)

**Fig. 6.1** (A) Twenty Continuous CV Responses of GCE (curve a), GCE/MWCNT (curve b and C) with 15 mM p-Aminobenzene Sulfonic Acid (p-SA) at Different Potential Windows (Set-I and Set-II), (B) GCE/MWCNT@SA-Oxid at a Scan rate 50 mV s$^{-1}$ in 0.1 M pH 7 PBS and (C) Plot of Anodic Peak Current vs Carbon Matrix for the Formation of Carbon@SA-Oxid system.

In continuation, another set of experiment (set-II) was performed, wherein, the GCE/MWCNT was subjected to p-SA electrochemical oxidation at wide potential window -0.7 to 0.7 V vs Ag/AgCl (Fig. 6.1 A, curve c). This time, rather to getting a well-defined redox peak, a broad and large current capacitive voltammetric response similar to one observing with poly aminobenzene sulfonic acid (PABS; Scheme 6.1 A and B) based electrochemical system was observed (Xi et al., 2016; Jin et al., 2005; Kumar and Chen, 2007a; 2007b). Based on the collective information from the above observations and literature on the quinone chemically modified electrodes (Vishnu and Kumar, 2016; Sornambikai and Kumar, 2012), it is speculated that quinone (possibly catechol or hydroquinone or resorcinol) like product unexpectedly formed on the MWCNT (Fig. 6.1 B, curve a) and metal impurity in MWCNT surface might be assisted the conversion reaction (Scheme 6.1 A-D). Hereafter, the oxidised p-SA modified electrode is designated as GCE/MWCNT@SA-Oxid, where SA-Oxid = Oxidized product
of SA. The redox peak obtained with GCE/MWCNT@SA-Oxid is adsorption-controlled in nature (peak current vs scan rate is linear (Fig. 6.2 A-B) and pH dependent characteristic (slope of plot of peak potential vs pH is $-45 \text{ mV pH}^{-1}$) (Fig. 6.2 C-D).

![Graphs](image)

**Fig. 6.2** (A) Effect of Scan rate (5-400 mVs$^{-1}$) on the CV of GCE/MWCNT@SA-Oxid in pH 7 PBS and (B) Plot of log $i_{pa}$ vs logv. (C) Effect of Solution pH (4−11) on the CV Response of GCE/MWCNT@SA-Oxid at a Fixed Scan rate of 50 mV s$^{-1}$ and (D) Plot of $E_{pa}$ vs pH. [Note: GCE/MWCNT@SA-Oxid = GCE/MWCNT@HQ].

6.3.2  Physico-chemical characterization of GCE/MWCNT@SA-Oxid

Fig. 6.3 A-C is a collective physicochemical characterization data of MWCNT@SA-Oxid system. Specific increment in the intensity ratio of D (disordered graphitic structure, sp$^3$ carbon) and G (graphitic structure, sp$^2$ carbon) bands, $I_D/I_G$ from 0.52 to 0.65 after the SA-oxidation on GCE/MWCNT surface was noticed (Fig. 6.3 A). This observation indicates occurrence of several sp$^3$ bonds, presumably carbon-oxygen...
functional groups like >C=O, -C-O-C– and –COOH etc, on the modified electrode surface (Vishnu and Kumar, 2016). In order to understand the interaction between the SA and carbon nanotube, MWCNT@SA-Oxid, MWCNT and naked were subjected to XRD analysis. As can be seen in the Fig. 6.3 B, several diffraction peaks of the SA at 2θ = 18.5°, 21.58° and 23.48° were retained with the MWCNT@SA-Oxid* hybrid sample without any alternation in the 2θ values. This observation supports the presence of SA species on the hybrid carbon nanotube matrix. Existence of the carbonyl functional group (1726.3 cm\(^{-1}\)) with the hybrid material was confirmed by FTIR/KBr characterization (Fig. 6.3 C, curve b). In further, IR peaks appeared at 2648.26 and 1932.67 cm\(^{-1}\) due to the benzene-substitution groups in p-SA (Donald et al, 2008), were disappeared after the electrochemical preparation supporting the molecular transformation reaction occurred on the MWCNT surface (Fig. 6.3 C, curve c).

![Fig. 6.3 Comparative Raman (A), XRD (B) and FTIR (C) Response of Various Systems.](image)

Fig. 6.4, shows comparative TEM photographs of MWCNT@SA-Oxid prepared at set-I (15.54 Å) and set-II (24.36 Å) conditions showed different sized MWCNT diameters (Gayathri et al., 2015). Based on the observation of large tube diameter size (Fig. 6.4 A) and high-capacitive current response (Fig. 6.1 A, curve c), it is postulated
that set-II based preparation procedure led thick polyaniline (PANI) like polymer formation (PABS) on the surface (Scheme 6.1 B) (Gayathri et al., 2015; Vishnu et al., 2013), whereas, set-I (Fig. 6.4 B) based preparation condition resulted in molecular transformation reaction (Fig. 6.1 B, curve a; Scheme 6.1 D).

Fig. 6.4 TEM Images of (a) MWCNT@poly-SA, (b) MWCNT@HQ, (c) MWCNT with Insets of Cartoons of Respective Systems.

Unfortunately, since the amount of SA-Oxid product formed is very less (~ng), it is not practically viable to extend for NMR characterization. Alternately, in-situ quartz crystal micro-balance experiment was carried-out similar to Fig. 6.1 A, curve b (set-l experiment) to elucidate the molecular transformation pathway of the p-SA on pristine-MWCNT. Fig. 6.5 A is in-situ CV response of EQCM-Au/MWCNT working electrode with 15 mM of p-SA at \( v = 50 \text{ mV s}^{-1} \). Due to noisy response, first four CV/in-situ EQCM responses were taken for molecular mass analysis as per our previous work (Sornambikai and Kumar, 2012). From the slope \((d(\Delta m)/dQ)\) of plots \( \Delta m \) vs \( Q \) obtained from in-situ CV cycles 3\(^{rd}\) and 4\(^{th}\) (Fig. 6.5 B-D), molecular weight of the intermediate species \((M_w = d(\Delta m)/dQ \times F, \text{ where } F = \text{Faraday constant})\) involved in the p-SA molecular transformation reaction was indirectly calculated as \(77.8 \pm 0.5 \text{ g mol}^{-1}\) and \(110.3 \pm 0.5 \text{ g mol}^{-1}\). These values are corresponding to the molecular species of benzene \((M_w = 78)\) and dihydroxy benzene (i.e., 1,2-(catechol) or 1,3-(resorcinol) or 1,4-dihydroxy benzene (hydroquinone)) \((M_w = 110)\) respectively.
To confirm the product, a methanolic extract of MWCNT@SA-Oxid obtained by sonication followed by 0.5 micron filtration, was subjected to GC-MS experiment. As can be seen in Fig. 6.6, a specific peak corresponds to molecular weight 110.26 was obtained for the major GC fraction (retention time 15.47 min), which authentically confirms the dihydroxy benzene formation occurred on MWCNT.

Meanwhile, to substantiate the finding, naked isomers of dihydroxy benzene isomers such as catechol (Fig. 6.7 A, curve a), resorcinol (Fig. 6.7 B, curve a) and hydroquinone (Fig. 6.1 B, curve b) were also subjected to CV studies with
The redox peak obtained with HQ ($E_{1/2} = 81\pm5$ mV vs Ag/AgCl) is closely matching with the $E_{1/2}$ value ($80\pm5$ mV vs Ag/AgCl) of GCE/MWCNT@SA-Oxid system (Fig. 6.1 B, curve a). Thus, it is evident that in set-I potential window, p-SA gets electro-oxidized as hydroquinone unexpectedly on GCE/MWCNT surface. Hereafter, the GCE/MWCNT@SA-Oxid is re-designated as GCE/MWCNT@HQ.

As given in Scheme 6.1 C and D, it is proposed that upon the CV potential cycling experiment, p-SA gets involved in deamination and desulfonation reactions (positive side at 0.4 V), which led to the formation of benzene as an intermediate that subsequently electro-oxidized as HQ via Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + 2\text{OH}^-$) utilizing the 2.1% iron impurity in the MWCNT (negative side at -0.4 V vs Ag/AgCl) (Vishnu and Kumar, 2016), wherein, H$_2$O$_2$ is in-situ generated via dissolved oxygen reduction reaction as per our previous report (Scheme 6.1 C). Although exact detail for the selective molecular conversion is unknown, it is likely that there is some memory effect happened on the conversion reaction of benzene to hydroquinone at MWCNT surface (Vishnu and Kumar, 2016). In-situ EQCM experiment confirmed the formation of the benzene as an intermediate product in the overall reaction (Fig. 6.5 C; Scheme 6.1 C). As control experiments, following p-SA electrochemical reactions were performed at;
(i) N\textsubscript{2} de-aerated pH 7 PBS; in aim to avoid formation of H\textsubscript{2}O\textsubscript{2} at negative side (Scheme 6.1 E) and (ii) 500 µM H\textsubscript{2}O\textsubscript{2} spiked N\textsubscript{2} gas purged pH 7 PBS solution (as a simulated condition) (Scheme 6.1 G). There was no formation of HQ redox peak in the case (i) condition (Fig. 6.7 C, curve a), whereas, intense appearance of redox peak was obtained with the H\textsubscript{2}O\textsubscript{2} spiked sample (case –ii) (Fig. 6.7 C, curve b). Meanwhile, to support the iron role, lower and no iron containing carbon materials such as purified MWCNT ([Fe] = 0.6 wt.%), graphite nanopowder ([Fe] = 0.22 wt.%) and carbon nanofiber ([Fe] = 0 wt.%), were also subjected for p-SA electrochemical reaction (Fig. 6.1 C; Scheme 6.1 F). Results of these experiments showed either poor or no HQ product formation supporting the key role of the iron impurity in this work. Finally, ortho (Fig. 6.7 A, curve b) and meta (Fig. 6.7 B, curve b) isomers of SA were also subjected to electrochemical reactions on pristine-MWCNT. Formation of multiple surface confined peaks, which are due to the formation of catechol and resorcinol like products respectively on the surface, were observed. Note that control CV experiments of GCE/MWCNT with naked catechol (Fig. 6.7 A, curve a) and resorcinol (Fig. 6.7 B, curve a) were yielded redox peaks very closer to the respective quinone peak potentials of ortho-SA (Fig. 6.7 A, curve b) and meta-SA (Fig. 6.7 B, curve b) modified electrodes confirm the electrochemical transformation products. A pre-peak observed with all the quinones (A1'/C1’, A2'/C2’ and A3'/C3’) on GCE/MWCNT is due to the redox features of the quinones at energetically different carbon sites similar to one observed with activated carbon electrode surface (Kumar et al., 2010; Kumar and Swetha, 2010).

In order to understand the influence of solution pH, electrochemical formation of GCE/MWCNT@HQ (at restricted potential window) were investigated at four different electrolyte solutions like pH 2 KCl-HCL, 0.1 M NaCl, pH 7 PBS and 0.1M NaOH. Three different isomeric precursors, para-, meta- and otho-SA were subjected to the electro-analysis. After the preparation, the “as prepared electrodes” were tested uniformly in a pH 7 PBS as in Fig. 6.8. Except pH 7 PBS, all other electrolyte solutions failed to show any marked redox signal for the quinone formation. The isomers showed appreciable redox response/s at pH 7 PBS due to formation of single and/or mixture of quinones like product/s such as 1,2 or 1,3 or 1,4 dihydroxy benzene derivatives on MWCNT (Fig. 6.8 G-I). The capacitor like CV responses noticed with the pH 2 KCl-HCl (Fig. 6.8 A-C), 0.1
M NaCl (Fig. 6.8 D-F) and 0.1 M NaOH (Fig. 6.8 J-L) mediums are due to the response of polyaniline like product formation.

**Fig. 6.8** CV Responses of Various SA Isomers Modified GCE/MWCNT Electrodes Prepared at Different Electrolyte Condition, in pH-7 0.1M PBS at a Scan rate 50 mV s⁻¹.

### 6.3.3 Electro catalysis of GCE/MWCNT@HQ towards NADH

Fig. 6.9 (A-C) is the electrochemical behaviour of the GCE/MWCNT@HQ modified electrode towards NADH oxidation in pH 7 PBS. With respect to the unmodified electrode (Fig. 6.9 A, curve c), the chemically modified electrode showed about 150 mV reduction in the oxidation potential and threefold increase in the NADH oxidation current was noticed (Fig. 6.9 A, curve b). Amperometric $i-t$ response of the modified electrode at a fixed applied potential ($E_{app}$= 0.15 V vs Ag/AgCl) for continuous
spikes of 50µM NADH showed a linear increase in the current signal up to 500 µM with sensitivity value 0.029 µA µM⁻¹ (Fig. 6.9 B, curve a). The GCE/MWCNT showed about 3-5 times lower current signals than that of the optimal electrode (Fig. 6.9 B, curve b). The GCE/MWCNT@HQ sensor showed tolerable to various co-existing biochemicals (Fig. 6.9 C). Observed sensitivity and selectivity values are superior than that of the other quinone based chemically modified electrodes used for NADH sensing (Dey et al., 2010; Kumar and Swetha, 2010; Wang et al., 2012; Maleki et al., 2012-Table 6.1).

**Fig. 6.9** (A) Comparative CV Responses of GCE/MWCNT@HQ without (curve a) and with 1 mM of NADH (curve b) and GCE/MWCNT with 1 mM NADH (curve c) in pH 7 PBS at v = 50 mV s⁻¹ ; (B & C) Amperometric I-T Responses of GCE/MWCNT@HQ (curve a) and GCE/MWCNT (curve b) with Continuous Spikes of 50 µM of NADH (B) or Other Interfering Chemicals (C) at an Applied Potential (E_{app}) of 150 mV vs Ag/AgCl in pH 7 PBS.

**Table 6.1** Comparison of the Analytical Performance of GCE/MWCNT@HQ for the Electrochemical Determination of NADH by Various Quinone Based Chemically Modified Electrodes.

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<th>S. No</th>
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<th>Sensitivity (µA/µM)</th>
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</tr>
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<td>The present work</td>
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6.4 Conclusion

Electrochemical oxidation/reduction of SA isomers at restricted potential window, -0.4 to 0.4 V on MWCNT modified glassy carbon electrode resulted in formation of highly redox active respective surface-confined quinones as a sole product. It was found that SA isomers get involved in deamination and desulfonation reactions followed by electro-Fenton based OH\(^*\) addition reaction upon the potential cycle experiment. The MWCNT@HQ prepared by new strategy showed highly stable and efficient electro-catalytic oxidation and sensing response to NADH without interference from common co-existing biochemicals. The result can help to develop a high redox active quinone modified electrode suitable for battery, electrochemical, electro-catalytic and sensor applications. Overall, observation of simple and selective oxidation of sulfanilic acid isomers to surface confined quinones is a new and novel observation in this work.