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Supplementary Information

In-situ Monitoring of Electrochemical Reactions Through CNTs-assisted Paper Cell Mass Spectrometry

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Supplementary Information 1

Mass spectrometery:

All the experiments were performed using an ion trap LTQ XL with the following mass spectrometric conditions. Source voltage: 0-6 V. This was applied through an external power supply, and was connected to the silver electrodes. As it is a two electrode system, the positive 0-6 V was applied to anode and the opposite polarity was applied to the cathode, from the same power source. Capillary temperature: was set at 150 ˚C (the temperature was set in the low range in order to avoid heavy fragmentation). Capillary and tube lens voltages were set at 0 V to avoid further fragmentation inside mass spectrometer. The sheath gas flow rate was also set to zero. All mass spectra correspond to an average of 25 scans. The identity of each species was confirmed by collision-induced dissociation. Three electrode experiments were performed to confirm the electrochemical events.

Supplementary Information 2

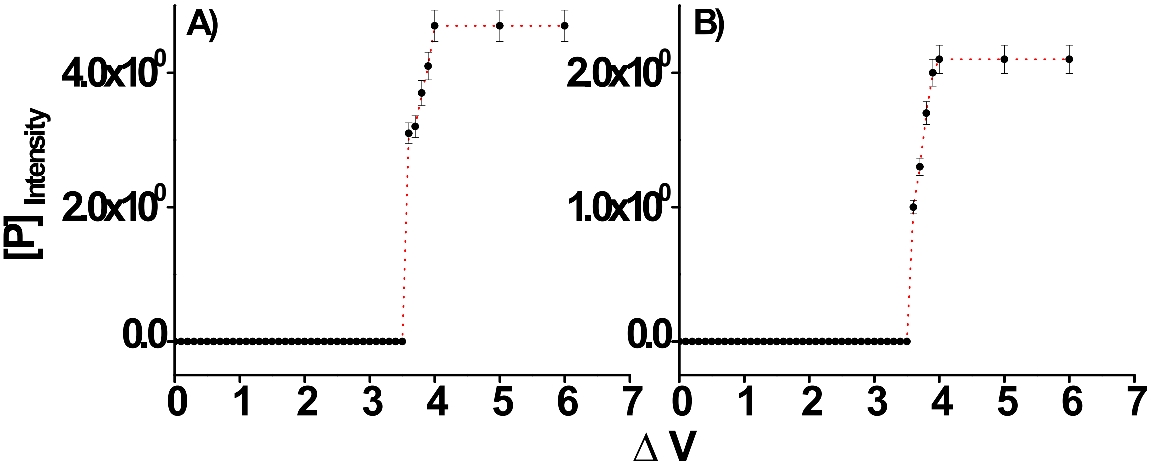

Figure S1. Product ion intensity - cell potential profile of A) cysteine and B) glutathione.

Supplementary Information 3

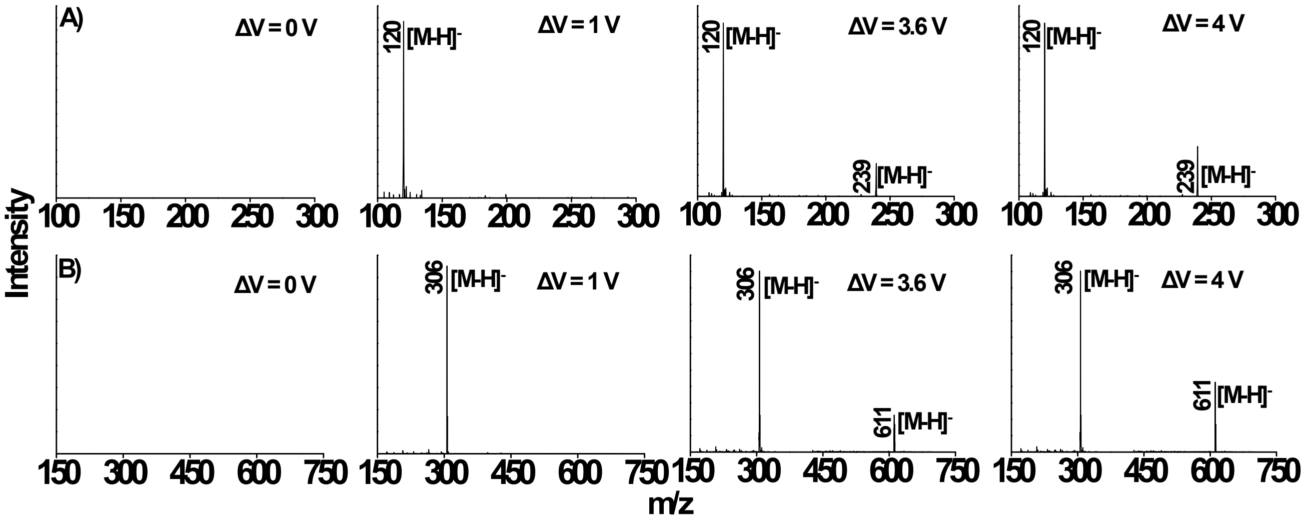

Figure S2.A) Mass spectra of cysteine (in methanol:water solvent mixture with KCl as an electrolyte) at different cell potentials, and B) Mass spectra of glutathione (in methanol: water solvent mixture with KCl as an electrolyte) at different cell potentials.

Supplementary Information 4

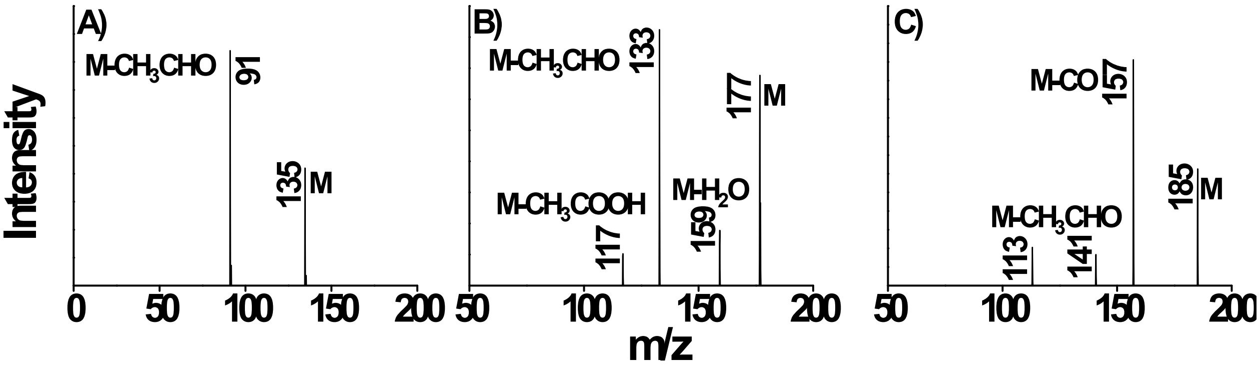

Figure S3. MS^2 spectra of A) benzene acetic acid, B) mesitylene acetic acid and C) naphthalene acetic acid.

Supplementary Information 5

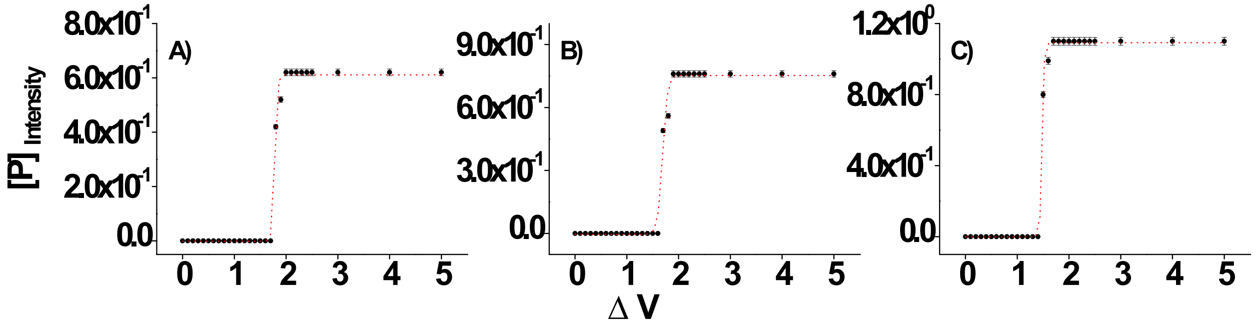

Figure S4. Product ion intensity - cell potential profile of A) benzene, B) mesitylene and C) naphthalene.

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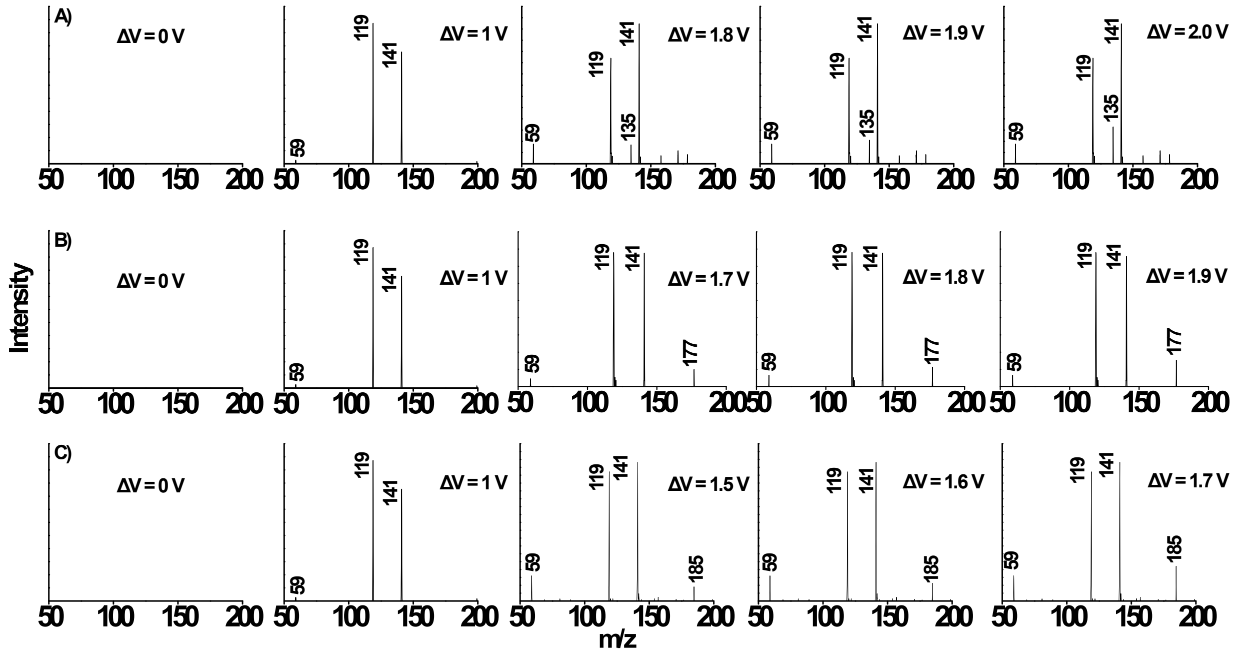

Figure S5. Mass spectra of A) benzene (in acetic acid solvent with sodium acetate as an electrolyte) at different cell potentials, B) mesitylene (in acetic acid solvent with sodium acetate as an electrolyte) at different cell potentials and C) naphthalene (in acetic acid solvent with sodium acetate as an electrolyte) at different cell potentials.

Supplementary Information 7

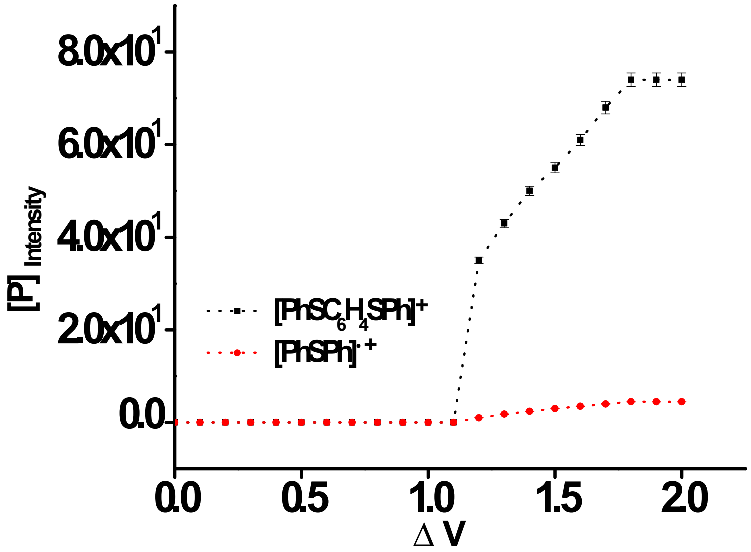

Figure S6. Product ion intensity-voltage profile for the electrochemical oxidation of diphenyl sulfide.

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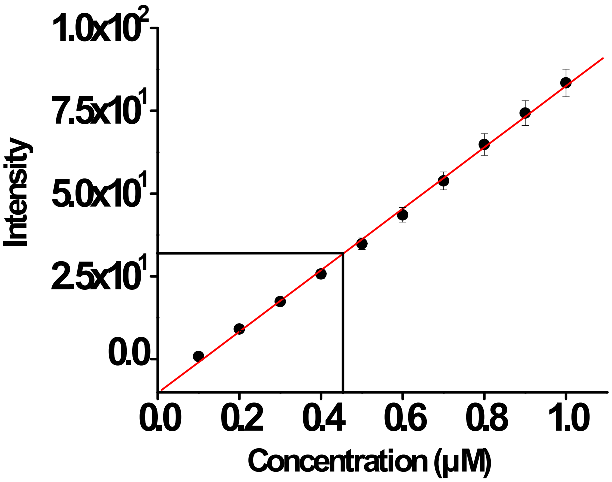

Figure S7. Intensity – concentration profile for glucose to saccharic acid oxidation.

Quantitation of glucose in blood serum

Volume of blood serum used – 100 µL

Assuming that 1mole of glucose produces 1 mole of gluconic acid and 1 mole of saccharic acid according to the following equation,

$$C_6H_{12}O_6 \xrightarrow{O_2} C_6H_{12}O_7 + C_6H_{10}O_8.$$

Product ion intensity in the experimental result indirectly implies the amount of glucose in blood serum.

The experimental result indicates the presence of 0.45 µM of glucose in 100 µL volume of blood serum, which is in good agreement with the actual value.

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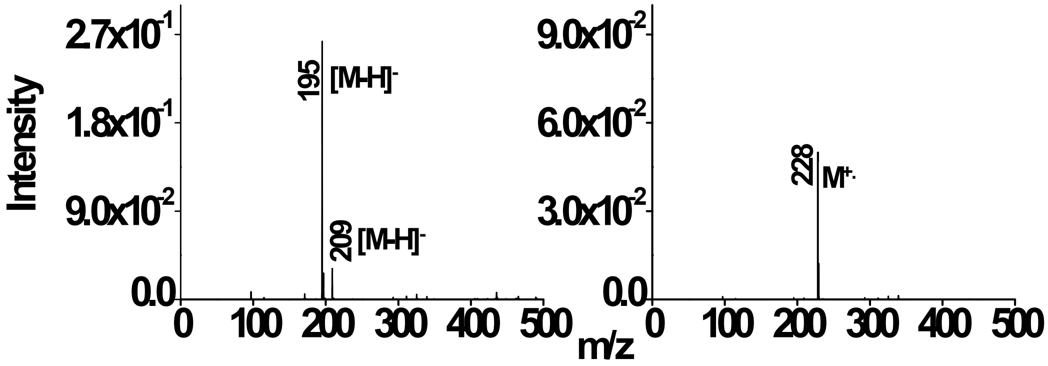

Figure S8. Electrochemical analysis of glucose (1 ppt) and 1, 2-benzanthracene (carcinogen) (10 ppm).

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Table S1: Observed and reported[1] oxidation and threshold potentials for in-situ electrochemical mass spectrometric measurement of polycyclic aromatic hydrocarbons.

No	Name of the chemical	Observed oxidation potential (V)	Threshold potential (V)	Observed mass speak (m/z)	Oxidation potential (V) from literature[1]
1	Benzene	1.57	1.80	78	1.80
2	Napthalene	1.26	1.50	128	1.31
3	Benzanthracene	0.99	1.20	228	0.92

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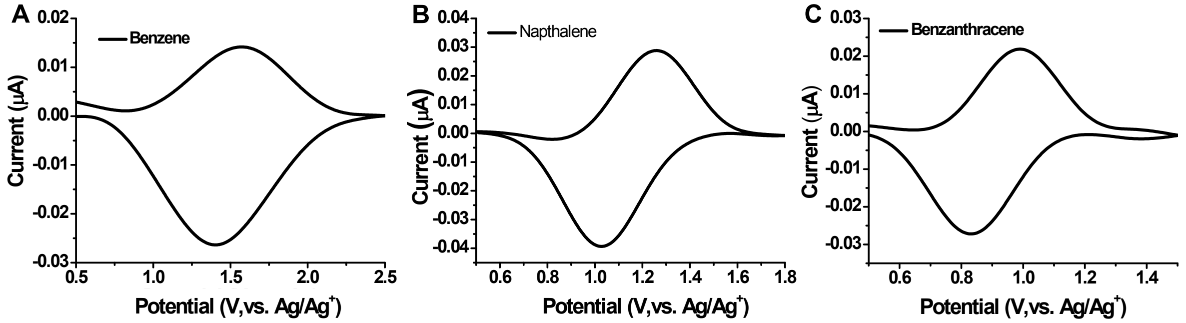

Figure S9. Cyclic voltammogram of A) benzene, B) napthalene, and C) benzanthracene during in-situ electrochemical mass spectrometry measurements.

References

1. Hoijtink, G. J., Oxidation potentials of conjugated hydrocarbons. *Recl. Trav. Chim. Pays-Bas Belg.* **1958,** *77*, 555-8.