Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Insights into carbon-nanotube-assisted electrooxidation of polycyclic aromatic hydrocarbons for mediated bioelectrocatalysis

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Materials and Methods

Mono-sodium phosphate monohydrate (NaH_2PO_4, ≥ 98%), di-sodium hydrogen phosphate heptahydrate (Na_2HPO_4, 98–102%), N,N-dimethylformamide (DMF, 99.9%), 1,4 naphthoquinone, N-methyl pyrrolidone (NMP), dichloromethane, potassium chloride (KCl, 99 %), D-(+)-glucose (≥ 99.5%), sodium hydroxide (>97%), naphthalene, pyrene, pyrene-NHS, perylene, coronene and sulfuric acid (95–98%) were purchased from Sigma Aldrich and used as received. Flavin adenine dinucleotide-dependent glucose dehydrogenase (FAD-GDH, 1150 U mg^{-1} solid) from *Aspergillus sp.* Sekisui Diagnostics (UK) and was used as received. The enzyme was stored at -20 °C. Distilled water was obtained by water purification to a resistivity of 15 MΩ cm using a Millipore Ultrapure system. Commercial grade multi-walled carbon nanotubes (MWCNTs, Ø = 9.5 nm, 1.5 µm length, ≥ 95% purity) were obtained from Nanocyl and used as received without purification. Glucose solutions were left to mutarotate overnight to β-D-glucose prior to use.

All experiments were conducted in Argon saturated phosphate buffer pH 7. Electrochemical measurements were recorded using a multichannel potentiostat Biologic® VMP3 running EC-lab software 10.39 and an Autolab potentiostat 100 (Eco Chemie, Utrecht, The Netherlands) running with Nova software (version 2.1). All experiments were performed in a three-electrode setup. A platinum wire was used as the counter electrode and all potentials were referred to the SCE electrode. Unless otherwise specified, the experiments were conducted at room temperature in 0.2 mol L^{-1}. NMR measurements were done with an Avance III 400 MHz instrument from Bruker. Glassy carbon electrodes (3 mm diameter) were functionalized in several steps. First, MWCNTs were dispersed in NMP (5 mg mL^{-1}) by sonication until a homogeneous black suspension was obtained. 20 µL of the MWCNT suspension was then deposited on the electrode to obtain a 5µm- thick film. After drying, the MWCNT deposits were modified with the polyaromatic hydrocarbons by drop casting 20 µL of a 10 mmol L^{-1} CH_2Cl_2. After an incubation/evaporation time over 10 min at room temperature in a fume hood, the electrodes were rinsed several times with H_2O and then dried and stored at 5°C until use.

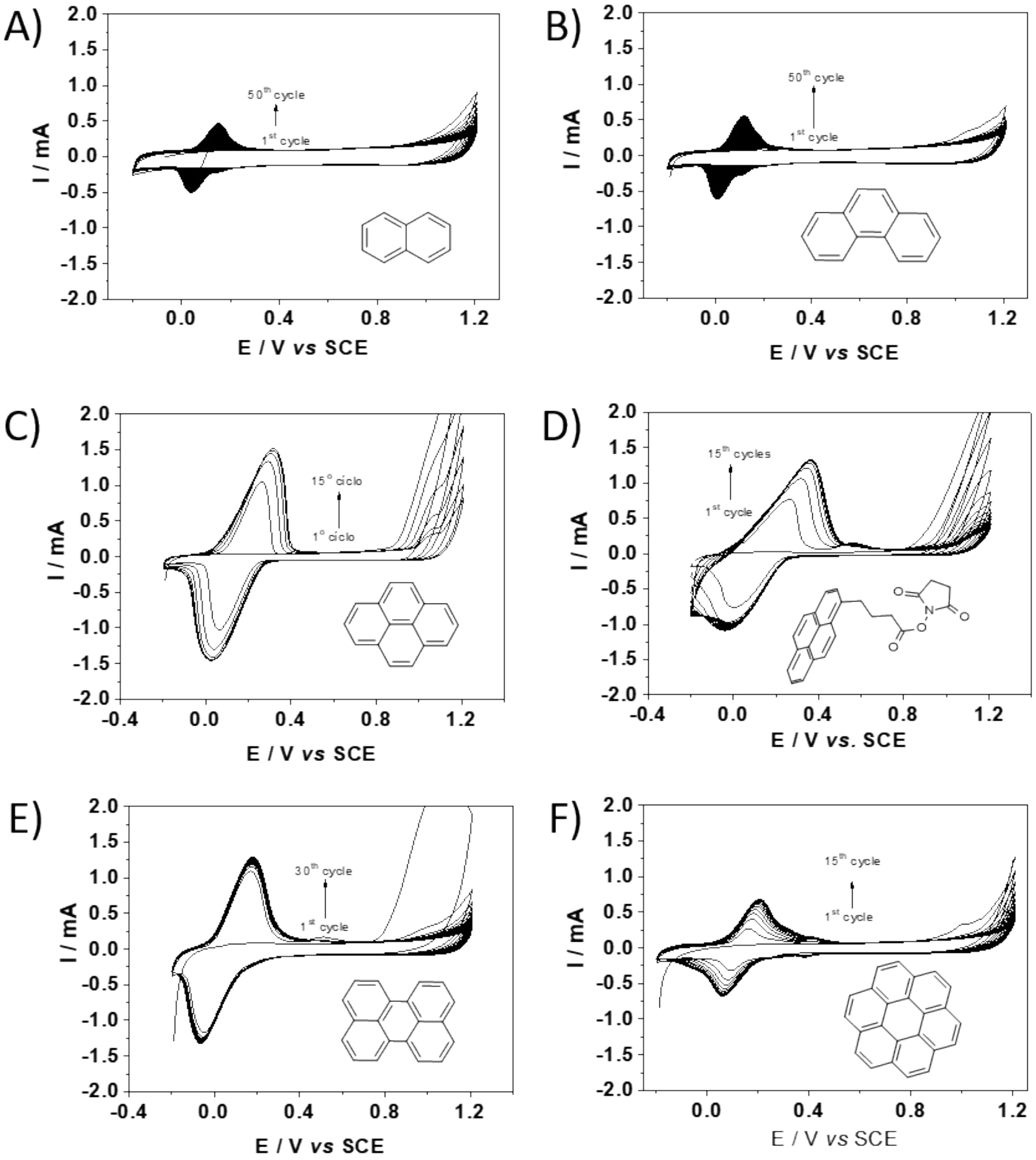


Figure S1: evolution of redox active species during electrochemical oxidation of a series of polyaromatic hydrocarbons, immobilized on MWCNT electrodes, in aqueous solution. (A) naphthalene, (B) phenanthrene, (C) pyrene, (D) pyrene-NHS, (E) perylene, and (F) coronene. The CVs were recorded in phosphate buffer solution (0.1 mol L^{-1}, pH 7) at a scan rate of 100 mV s^{-1}

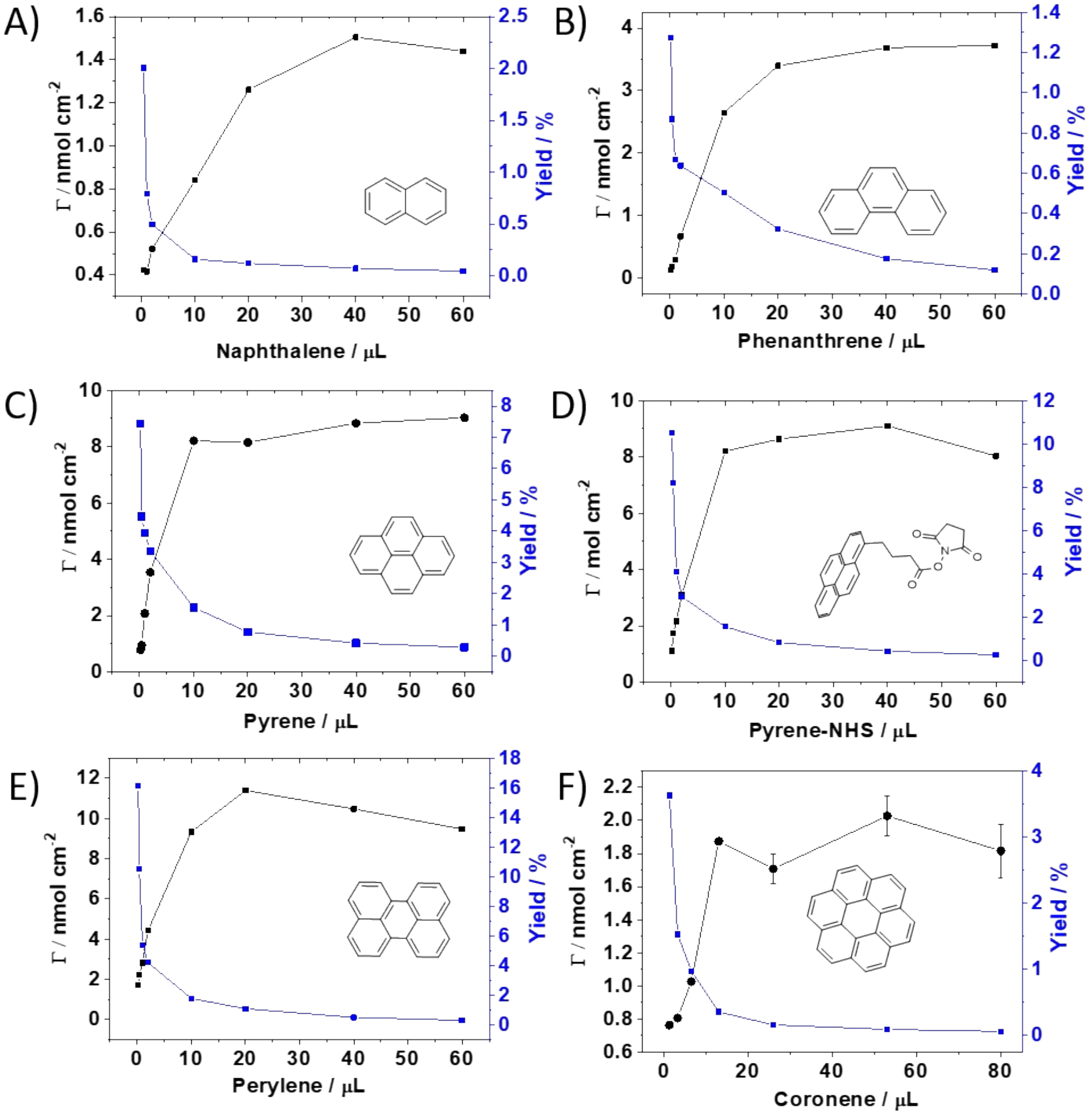
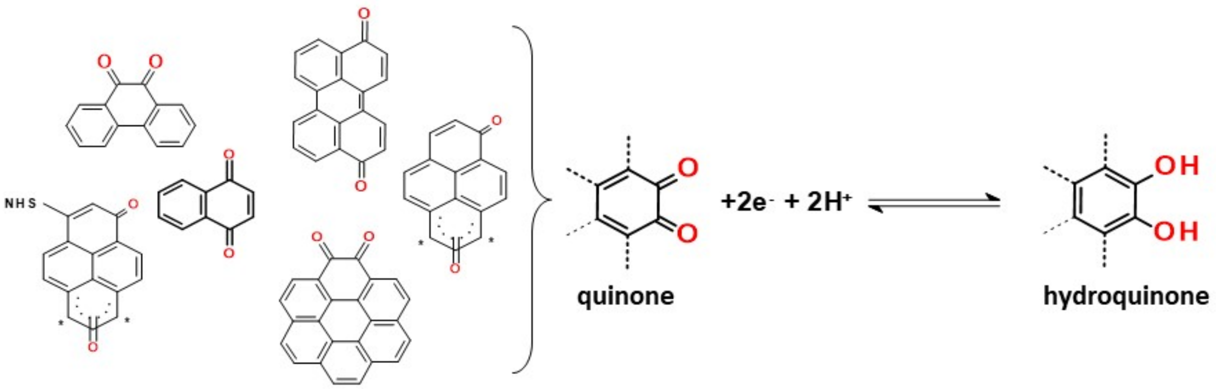


Figure S2: plot of electro oxidation yield and surface coverage as a function of the deposited polyaromatic hydrocarbons (10 mmol L^{-1} in CH_2Cl_2). (A) naphthalene, (B) phenanthrene, (C) pyrene, (D) pyrene-NHS, (E) perylene, and (F) coronene.



Scheme S1: redox equation of the electrosynthesized polyaromatic quinones for a 2 electron / 2 proton process.

Table S1: characteristic parameters of the studied polyaromatic hydrocarbons after electro oxidation.

	E^0_{app} V vs SCE (pH 7)	E^0_{app} V vs NHE (pH 7)	ΔEp (mV, pH 7)	Γmax (nmol cm^{-2})	pH dependence (mV per pH unit)
Naphthalene	-0.17 (+/- 0.02)	0.07	29	2.7 (+/-0.2)	54
Phenanthrene	-0.19 (+/- 0.02)	0.05	39	3.7 (+/-0.2)	54
Pyrene	-0.07 (+/- 0.02)	0.17	141	9 (+/-1)	53
Pyrene-NHS	-0.10 (+/-0.03)	0.14	116	8.15 (+/-2)	51
Perylene	-0.14 (+/- 0.02)	0.10	80	1.1(+/-2)	51
Coronene	-0.08 (+/- 0.02)	0.16	108	2.0(+/-0.2)	55

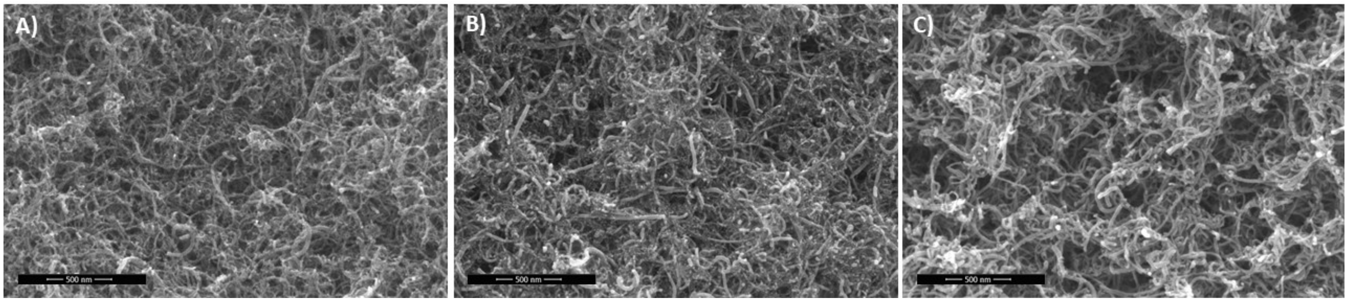


Figure S3: SEM images of A) CNT modified gassy carbon electrodes, B) CNT +pyrene modified gassy carbon electrodes, and C) CNT +pyrene modified gassy carbon electrodes after electro-oxidation at 1.2 V vs SCE and at pH 2.

^{1}H-NMR data

1,4-naphthoquinone: δ (ppm) = 8.084 (Hc, 2H, dd, J = 4 Hz), 7.76 (Hc, 2H, dd, J = 3Hz), and 6.98 ppm (He, 2H, s,)

Phenanthrene: δ (ppm) = 8.69 (He, d, 2H), 7.88 (Hb, d, 2H,), 7.73 (Ha, s, 2H), 7.65, (Hd, m, 2H), and 7.59 (Hc, m, 2H)

9,10-phenanthrenequinone: δ = 8.19 ppm (Hf, m, 2H, J = 8.9 Hz), 8.02 ppm (Hi, m, 2H, J = 8.9 Hz), 7.78 (Hh, m, 2H, J = 6.9 Hz), and 7.47 ppm (Hg, m, 2H, J = 7.9 Hz)

1,6-pyrenedione: δ (ppm) = 8.48 (Hd, d, 2H, J = 5.83 Hz), 7.85 (Hc, d, 2H, J = 6.03 Hz), 7.65 (Hb, d, 2H, J = 8.80 Hz), and 6.73 (Ha, d, 2H, J = 7.96 Hz)

1,8-pyrenedione: δ (ppm) = 8.63 (Hh, d, 2H, J = 0.80 Hz), 7.69 (Hg, d, 2H, J = 7.76 Hz), 7.52 (Hf, d, 2H, J = 6.80 Hz), and 6.67 (He, d, 2H, J = 7.88 Hz)

Pyrene-NHS: δ (ppm) = 8.28 (Hd, d, 1H, J = 7.32 Hz), 8.18 and 8.10 (Hc, Hg, Hh, m, 3H), 8.02 (He, s, 1H), 7.98 (Hf, Hi, dd, 2H, J = 6.12 Hz), and 7.88 (Ha, Hb, d, 2H, J = 6.08 Hz).

1,8-pyrenedione-NHS: δ (ppm) = 8.63 (Hk, Hl, s, 2H), 7.81 (Ho, Hp, d, 2H, J = 5.84 Hz), multiplett between 7.74 and 7.65 (Hn, 1H), and 6.60 (Hj, Hm, d, 2H, J = 8.76).

1,6-pyrenedione-NHS: δ (ppm) = 8.51 (Hr, Hv, dd, 2H, J = 6.08 Hz), multiplett between 7.74 and 7.65 (Hs, Hw, m, 2H), and 6.69 (Hq, Hu, dd, 2H, J = 8.04 Hz).

Perylene: δ (ppm) = 8.18 (Ha, d, 4H, J = 8.8 Hz), 7.67 (Hc, d, 4H, J = 8.8 Hz), and 7.71 (Hb, t, 4H, J = 7.5 Hz)

3,10-perylenedione δ (ppm) = 9.02 (Hf, d, 2H, J = 7.5 Hz), 8.69 (Hh, d, 2H, J = 6.0 Hz), 8.49 (He, d, 2H, J = 10.0 Hz), 8.00 (Hg, t, 2H, J = 7.5 Hz), and 6.97 (Hd, d, 2H, J = 10.0 Hz)

Coronene: δ (ppm) = 8.90 (Ha, s, 12H)

1,2-coronenedione: δ (ppm) = 9.06 (Hf and He, d, 4H, J = 8.9 Hz), 9.04 (Hc and Hd, d, 4H, J = 7,6 Hz), and 8.75 (Hb, d, 2H, J = 8.3 Hz)

1,10-coronenedione: δ (ppm) = 8.37 (Hg, s, 2H), 8.21 (Hk, d, 2H, J = 7,6 Hz), 8.15 (Hj, d, 2H, J = 9.6 Hz), 8.10 (Hi, d, 2H, J = 8.9 Hz), and 8.03 (Hh, t*, 2H, J = 8.3 Hz)

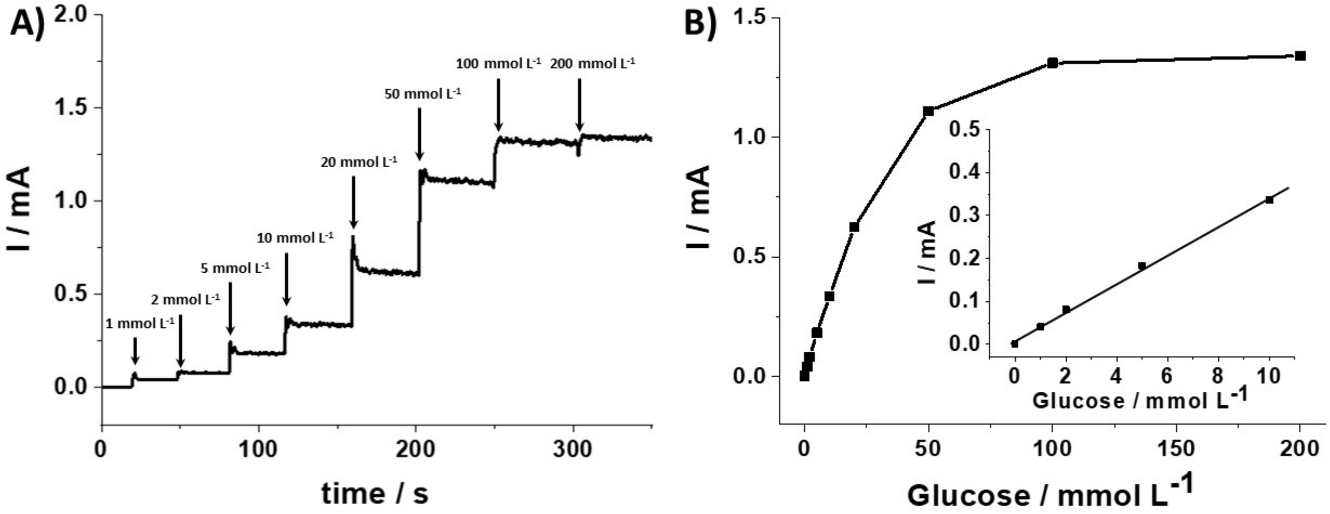


Figure S4: (A) Current changes after successive injections of glucose obtaining steady increasing concentrations. (B) Calibration curve from the data obtained in A). Inset: Linear part in the glucose concentration range between 0 and 10 mmol L^{-1}