Electronic Supplementary Information (ESI)

Electrochemical properties of vertically aligned graphenes: tailoring heterogeneous electron transfer through manipulation of the carbon microstructure

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Figure S1. Raman spectra of the various vertical graphene samples: V_1Graphene, V_2Graphene, V_3Graphene and V_4Graphene (A, B, C and D) respectively.

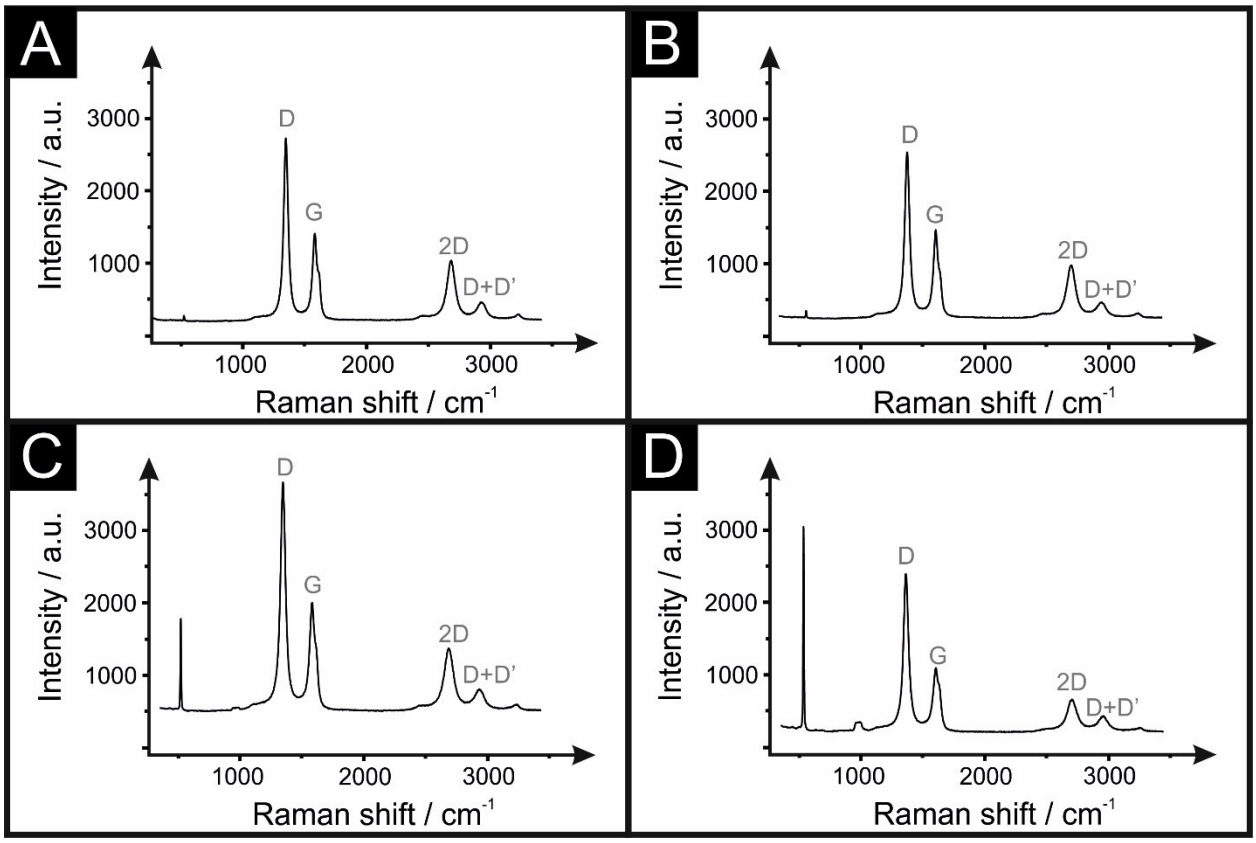

Table S1. Comparison of the Raman spectroscopy characterisation of the various vertical graphene samples, including positions of the D, G and 2D bands (PD, PG and P2D respectively), full width half-maximum (FWHM) of the D, G and 2D bands (WD, WG and W2D respectively), and intensity ratios.

	PD / cm^{-1}	**WD / cm^{-1}**	**PG / cm^{-1}**	**WG / cm^{-1}**	**P2D / cm^{-1}**	**W2D / cm^{-1}**	**I_D/I_G**	**$I_D/I_{D'}$**	**$I_{D'}/I_G$**	**I_{2D}/I_G**
V_1Graphene	1355.46	40.91	1586.96	42.46	2702.34	75.09	2.05	7.07	0.29	0.84
V_2Graphene	1355.50	40.07	1587.07	40.38	2702.40	75.05	2.05	6.61	0.31	0.81
V_3Graphene	1354.97	41.48	1587.57	42.29	2701.42	76.74	2.34	6.50	0.36	0.80
V_4Graphene	1354.75	42.06	1589.28	45.32	2701.0	80.88	2.48	7.52	0.33	0.62

Table S2. XPS analysis showing the composition of the V_1Graphene, V_2Graphene, V_3Graphene and V_4Graphene samples respectively.

Element	V_1Graphene	V_2Graphene	V_3Graphene	V_4Graphene
C1s C-C-C-H Graphite	284.58 (74.29)	284.56 (79.07)	284.57 (80.77)	284.6 (75.85)
C1s C-H	285.47 (10.43)	285.61 (11.29)	285.74 (12.3)	285.81 (13.53)
C1s -C-O, in phenolic, etheric, alcoholic	286.41 (5.63)	286.6 (4.89)		287.08 (4.68)
C -C=O- or -O-C=O	287.59 (1.3)	287.89 (1.45)	287.1 (3.57)	289.05 (1.51)
C Atomic %	91.65	96.7	96.64	95.57
O 1s -O-C (in phenolic, epoxy or ether)	531.79 (4)	531.83 (2.08)	531.65 (1.43)	531.79 (2.29)
	533.19 (4.35)	533.36 (1.22)	533.14 (1.93)	533.27 (2.14)
O1s Atomic %	8.35	3.30	3.36	4.43

Figure S2. AFM profile analysis of the V_1Graphene, V_2Graphene, V_3Graphene and V_4Graphene samples respectively.

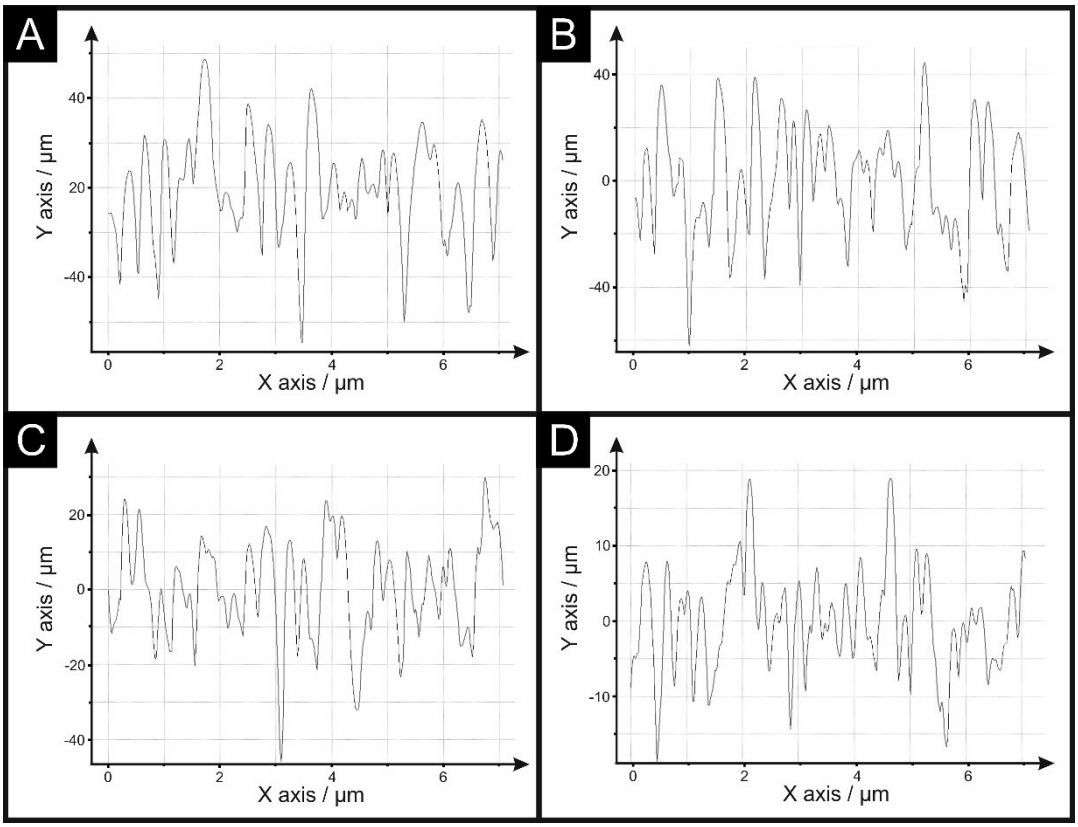

Table S3. AFM surface analysis of the various vertical graphene samples.

Sample	Average roughness (Ra) / nm	Root-mean-square roughness (Rq) / nm
V_1Graphene	17.65	23.01
V_2Graphene	16.74	20.23
V_3Graphene	10.52	13.10
V_4Graphene	5.15	6.67

Figure S3. Cyclic voltammetric responses recorded over a range of scan rates recorded using V_1Graphene, V_2Graphene, V_3Graphene and V_4Graphene (A, B, C and D respectively) with 1 mM RuHex in 0.1 M KCl (*vs*. SCE). Scan rate range varies from 15 to 400 mV s^{-1}.

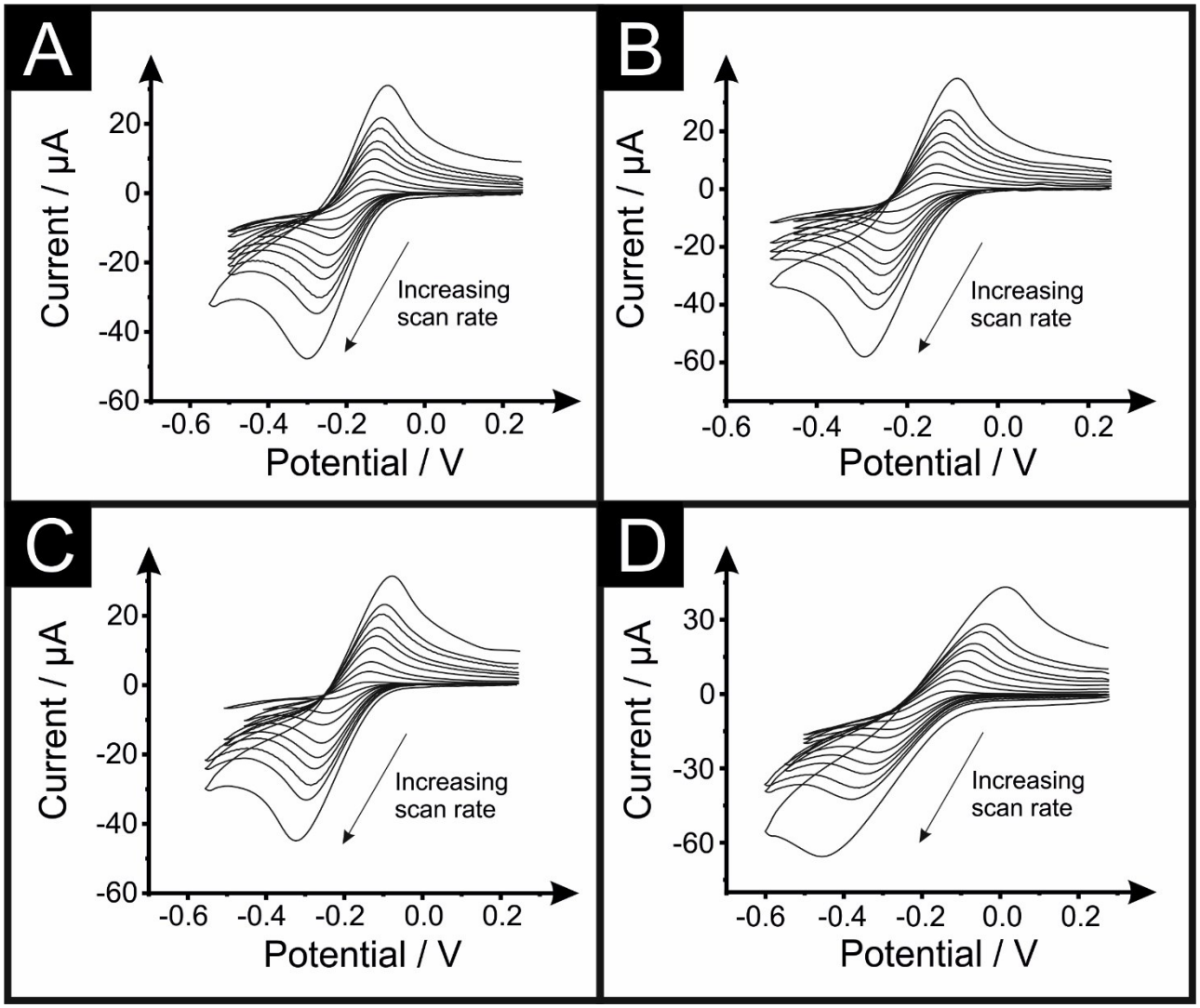

Figure S4. Cyclic voltammetric responses recorded over a range of scan rates recorded using V_1Graphene, V_2Graphene, V_3Graphene and V_4Graphene (A, B, C and D respectively) with 1 mM TMPD in 0.1 M KCl (*vs*. SCE). Scan rate range varies from 15 to 400 mV s^{-1}.

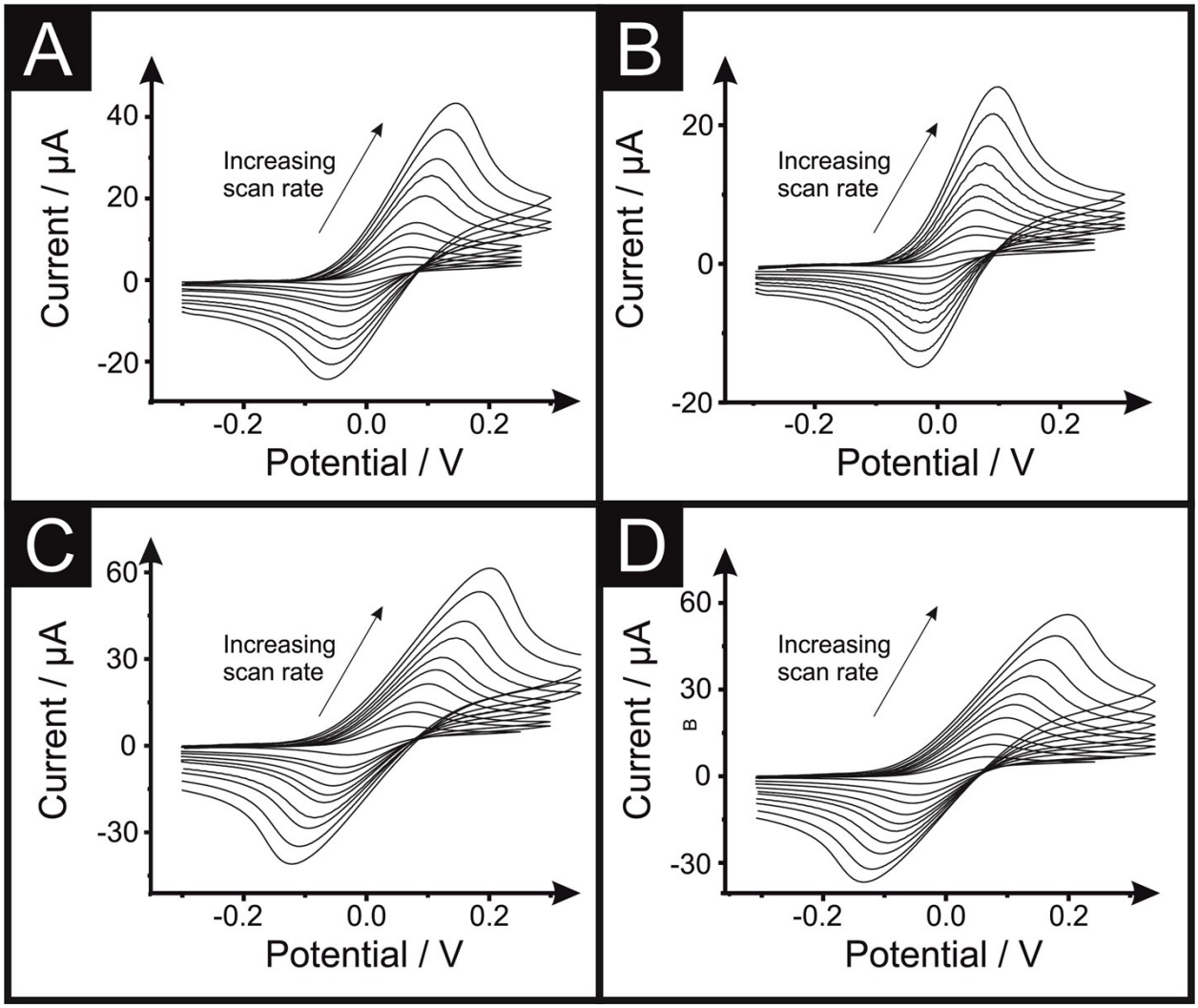

Table S4. Peak-to-peak (ΔE_P) separation and heterogeneous electron transfer rate constants (k^0_{eff}) values determined using 1 mM TMPD (*vs*. SCE).

	ΔEp / mV (@100 mV s^{-1})	**k^0_{eff} / cm s^{-1}**
EPPG	95.2	8.00×10^{-3}
V_1Graphene *	110.4	4.16×10^{-3}
V_2Graphene	87.9	5.47×10^{-3}
V_3Graphene	190.4	1.74×10^{-3}
V_4Graphene	200.2	1.28×10^{-3}
Quasi-G	136.7	3.25×10^{-3}
Mono-G	205.1	1.81×10^{-3}

** V_1Graphene values do not align to the perceived trend with this probe, likely due to the elevated presence of oxygen species on the sample's surface influencing the electrochemistry. This has been observed using mono-layer CVD graphene and graphene oxide with TMPD (see Refs. [53, 72] within the manuscript), which is unexpected given that it is an outer-sphere redox probe. Results and low oxygenated species contents are consistent in the other samples and they can therefore be directly compared.*