Supplementary material

Augmenting the performance of thermally deoxygenated graphite oxide supercapacitor electrodes using 6 M KOH electrolyte with K_3 $Fe(CN)_6$ redox additive.

Arsha M.S. and Biju V.*

Department of Physics, University of Kerala, Karyavattom, Thiruvananthapuram, Kerala, INDIA, Pin- 695581

E-mail:- bijunano@gmail.com

Synthesis of graphite oxide (GO)

The process involved mixing 3g of graphite powder with 70 ml of concentrated sulfuric acid (H_2SO_4) while stirring and keeping the temperature below 10°C using an ice bath. Then, 9 g of potassium permanganate ($KMnO_4$) was gradually added to the mixture while keeping the temperature below 20°C. The mixture was then stirred for 30 minutes in an oil bath maintained at 40°C. After this, distilled water was added, and the solution was stirred at 95°C for 15 minutes. To stop the reaction, hydrogen peroxide (H_2O_2) was added, causing the colour of the solution to change from dark brown to yellow. The resulting solution was left to settle overnight, and the product obtained was vacuum dried at 60°C to obtain GO.

Thermogravimetric analysis of GO

Fig. S1 depicts the TGA curve of graphene oxide (GO) under a nitrogen (N_2) atmosphere up to 800 ^{0}C. The TGA curve reveals three distinct stages: initially, around 10% weight loss is evident, attributed to the removal of water molecules. Subsequently, a sharp 25% decrease in weight percentage occurs, associated with the elimination of oxygen functional groups, such as hydroxyl (O-H) and carboxyl (-COOH) groups [1]. Beyond 275 ^{0}C, a slow decrease in weight loss is observed. This is primarily related to the elimination of remaining functional groups like

carbonyl (-C=O) and epoxy (C-O-C) groups, possessing high binding energy [2]. Beyond 500 ^{0}C, ~ 50% weight loss is observed. It is noteworthy that thermally deoxygenated GO beyond 500 ^{0}C Celsius may not be beneficial for electrode material purposes. Therefore, deoxygenation temperatures were selected at 100, 200, 300, and 400 degrees.

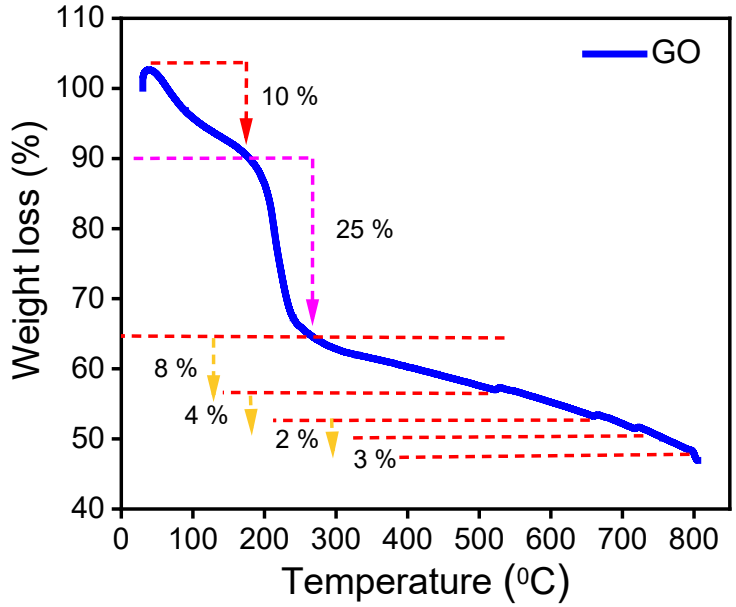

Fig. S1 TGA curve of graphite oxide (GO)

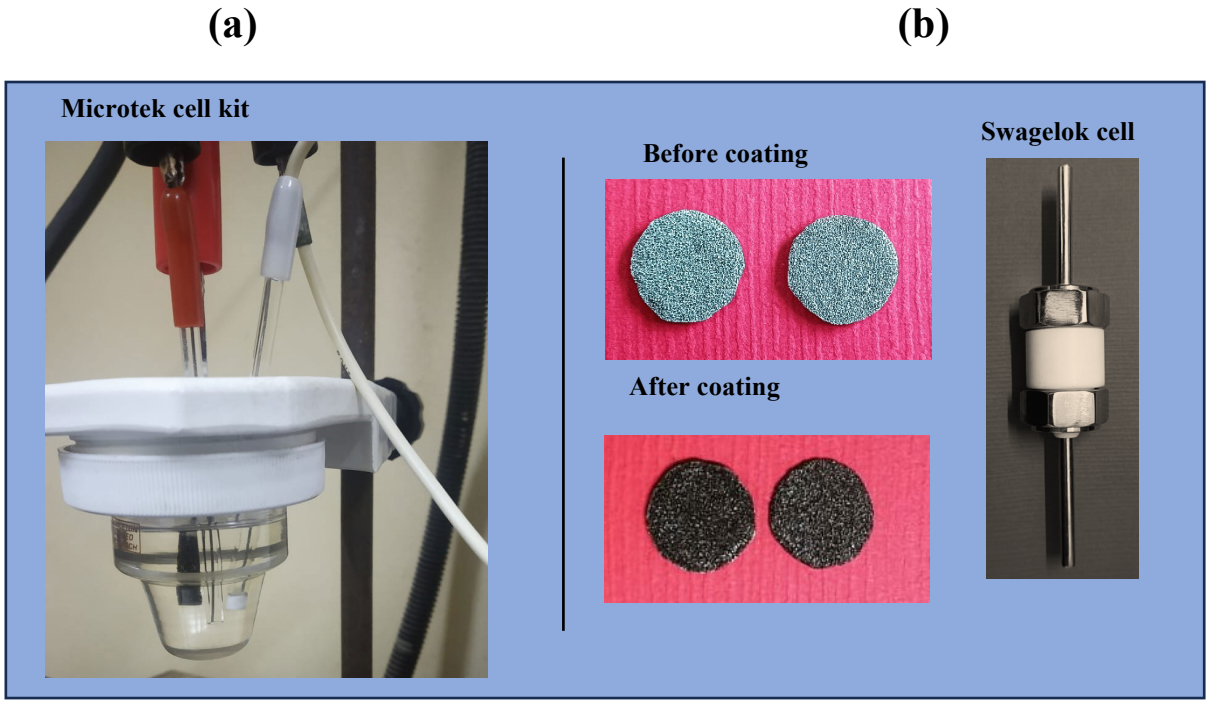

Fig. S2 (a) Microtek cell kit used for three electrode measurement, (b) Swagelok cell assembly used for two electrode configuration

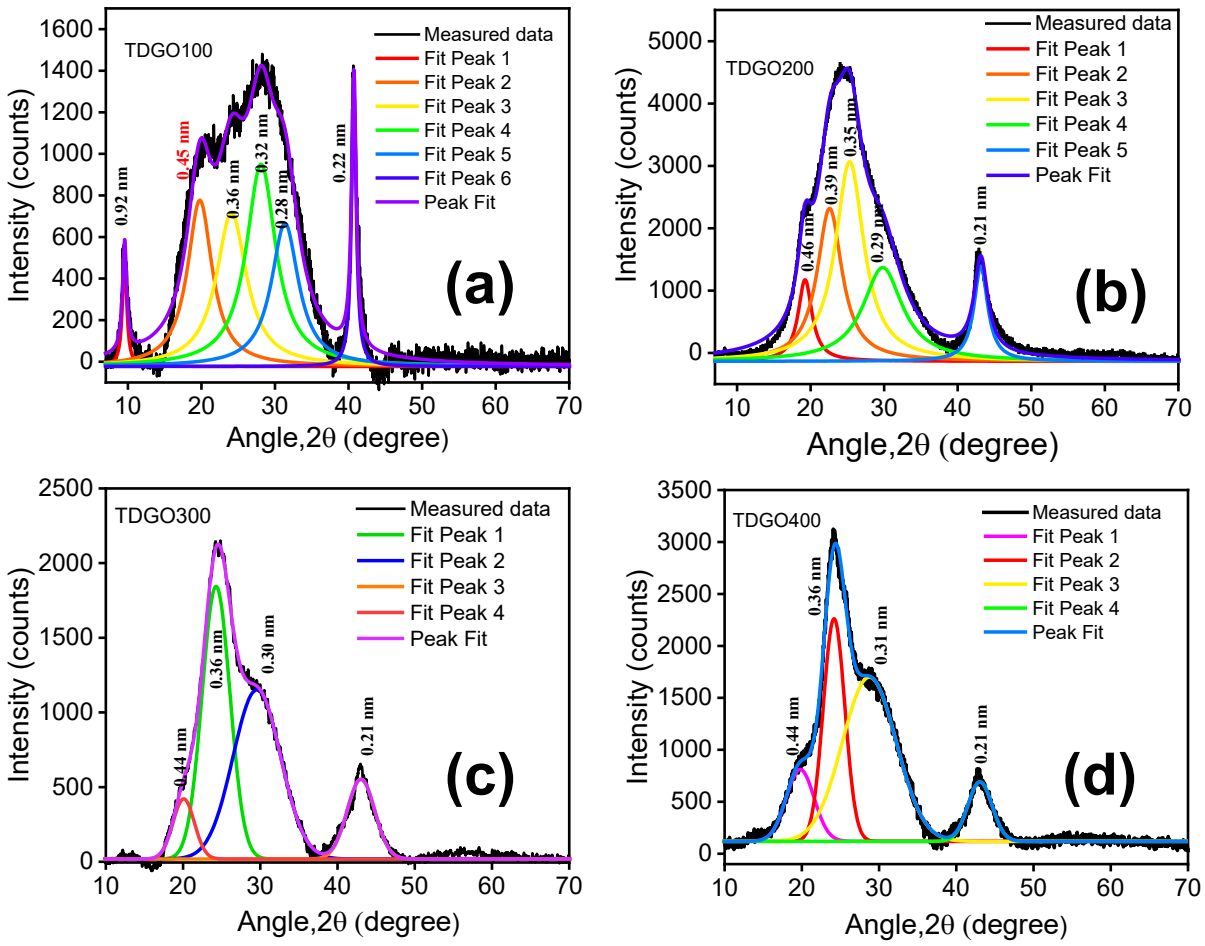

Fig.S3 3The results of (002) peak deconvolution of (a) TDGO 100, (b) TDGO 200, (c) TDGO 300 and (d) TDGO 400 samples.

Table S1 Result of (002) peak deconvolution

Sample code	2 Theta (degree)	Theta (radian)	d value (nm)	FWHM (degree)	D, layer stacking distance (Å)	N_L, number of layers
Graphite (GR)	26.3	0.23	0.34	0.37	218.13	65
GO	10.9	0.09	0.81	1.54	51.58	10
TDGO100	19.78	0.17	0.37	4.08	19.77	5
	24.08	0.21	0.32	4.98	16.31	5
	28.11	0.24	0.28	4.87	16.82	6
	31.35	0.27	0.22	4.49	18.38	7
TDGO200	19.24	0.16	0.46	2.27	35.51	9
	22.58	0.20	0.39	4.09	19.81	6
	25.31	0.22	0.35	4.69	17.36	6
	29.81	0.26	0.30	6.51	12.63	5
TDGO300	20.08	0.17	0.44	2.76	22.54	6
	24.27	0.21	0.36	3.61	22.52	7
	29.55	0.25	0.30	6.15	13.36	5
TDGO400	19.78	0.17	0.44	3.64	22.41	6
	24.17	0.21	0.36	2.75	29.13	8
	28.73	0.25	0.31	7.21	11.78	5

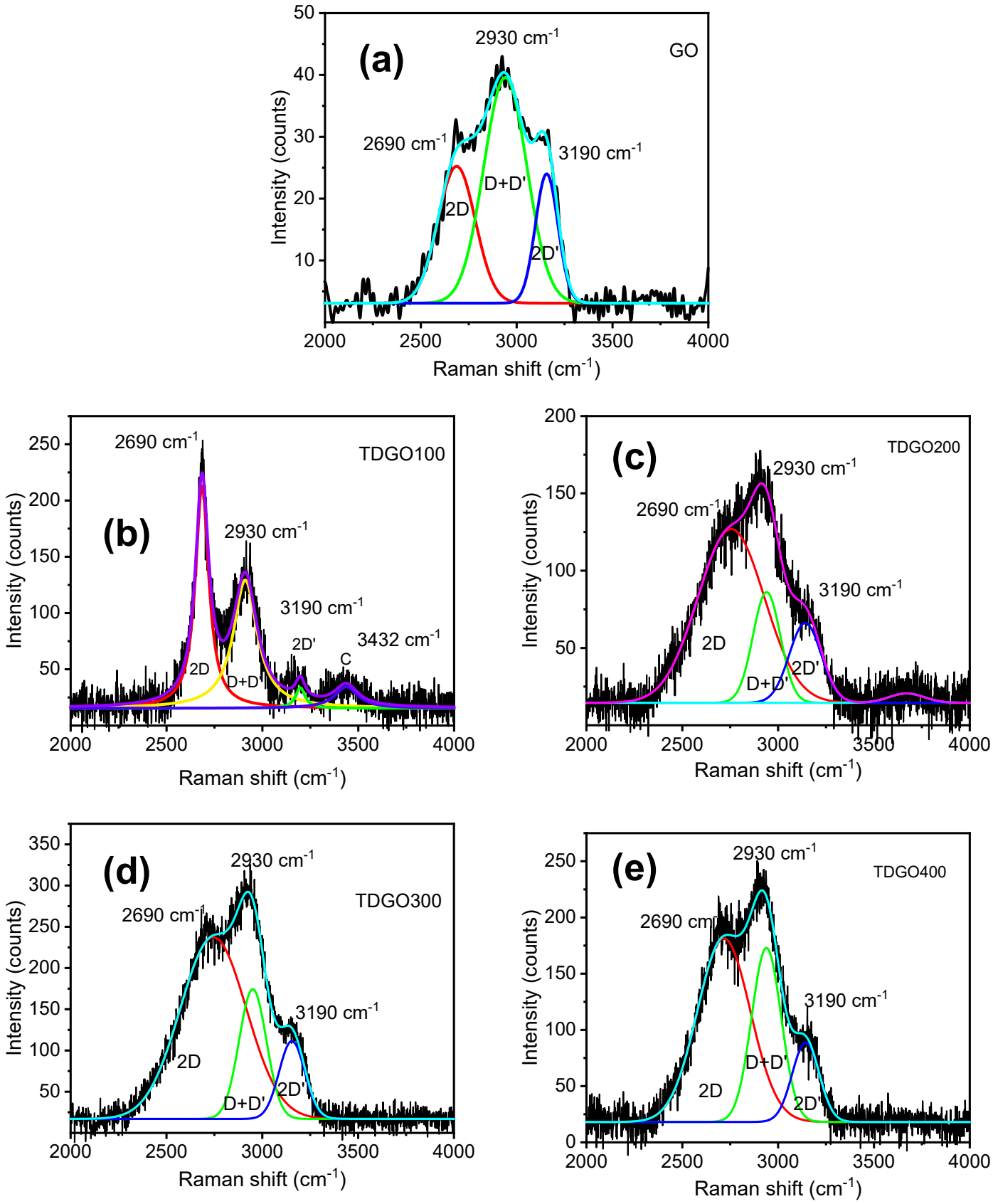

Fig. S4 Deconvolution of second order peak in (a) GO, (b) TDGO100, (c) TDGO200, (d) TDGO300, (e) TDGO400

Redox reactions during thermal deoxygenation and vacancy defects

During the thermal deoxygenation process, carbon atoms within the GO structure, in an oxidation state of +1 as found in epoxides and alcohols, undergo transformation. They change into two distinct forms: elemental carbon, with an oxidation state of 0, and carbon dioxide (CO_2), where the oxidation state increases to +4. Furthermore, the elimination of carbon atoms in the form of carbon monoxide (CO) and CO_2 results in vacancy defects. The respective redox equations can be written as follows [2].

$$2R_2COC\,^{(+1)}R_2 \rightarrow 3R_3C^{(0)} + 2R + C^{(+4)}O_2 \quad (1)$$

$$R_2COOCR_2 \rightarrow R_3C + R + CO \quad (2)$$

$$2R_2C{=}O \rightarrow R_2C + CO_2 \quad (3)$$

The removal of one carbon atom per every two oxygen atoms from the GO network is observed in the redox equation. In the reaction producing, one carbon atom is removed per every oxygen atom. However, thermally deoxygenated GO (TDGO) with vacancy defects is superior to other RGOs as an electrode material for energy storage in supercapacitors since the holes increase the surface area and provide channels for the transport of ions.

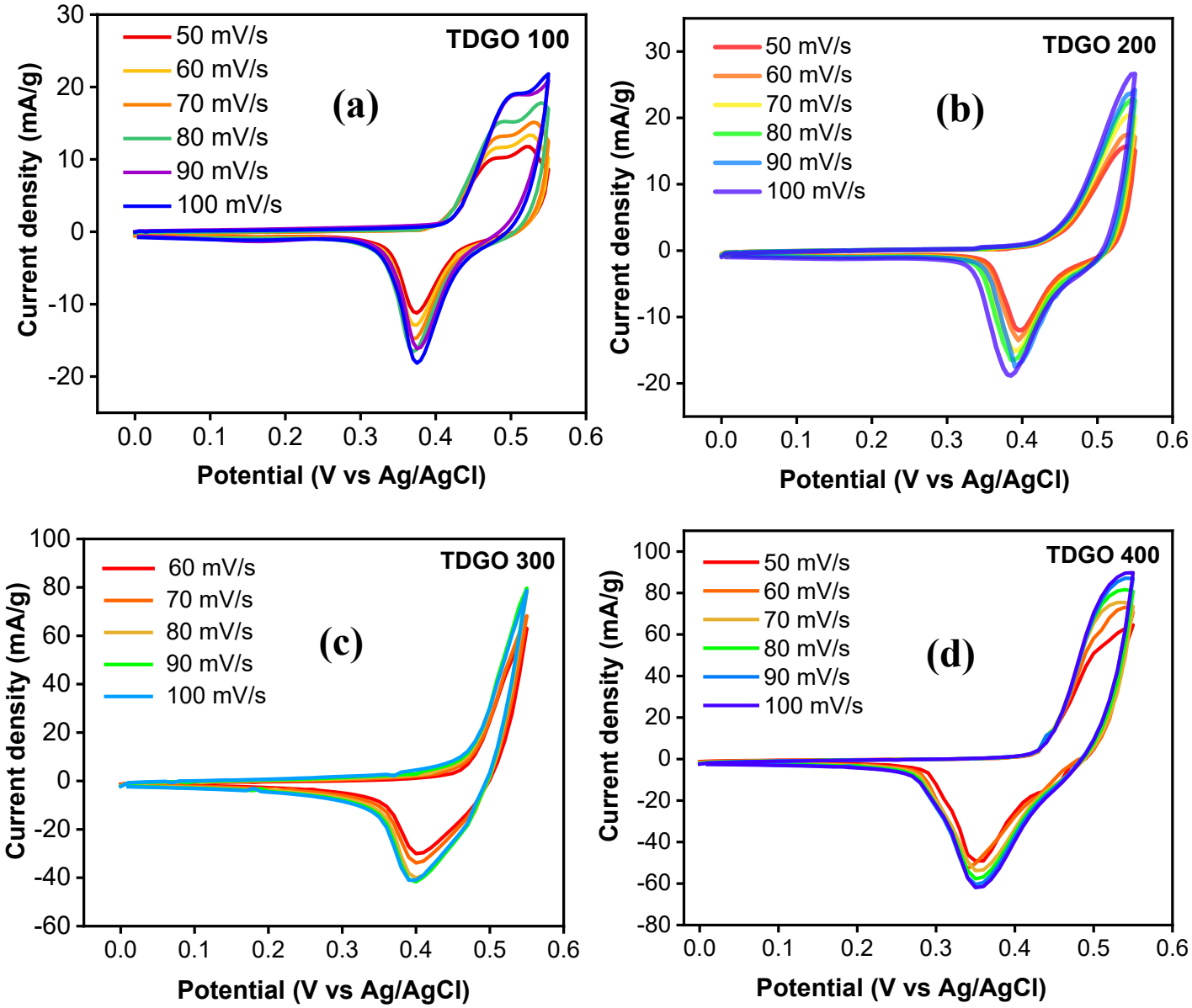

Fig. S5 Cyclic voltammogram of (a) TDGO100, (b) TDGO200, (c) TDGO300 and (d) TDGO400

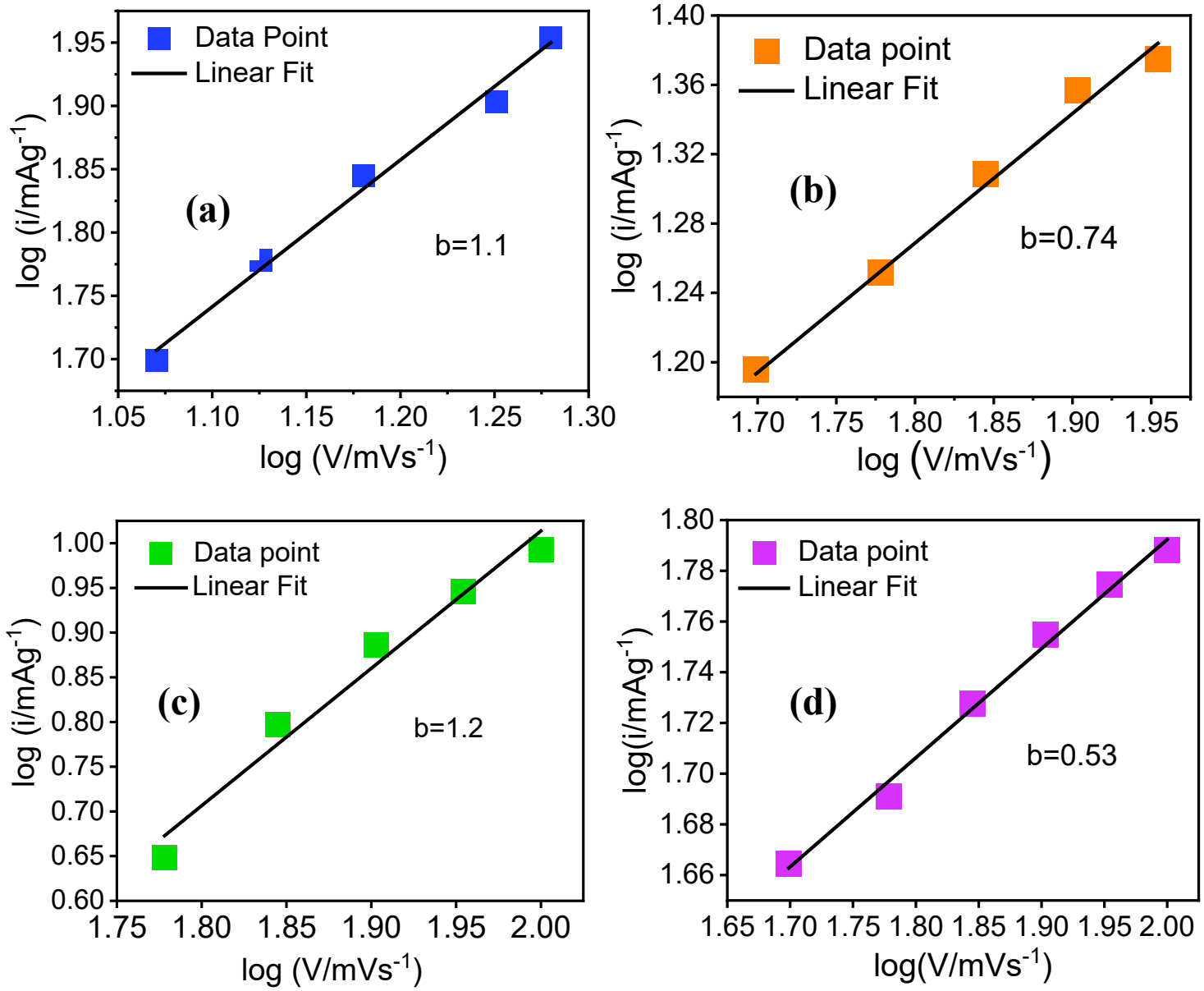

Fig. S6 logV vs Log i plot of (a) TDGO100, (b) TDGO200, (c) TDGO300, (d) TDGO400

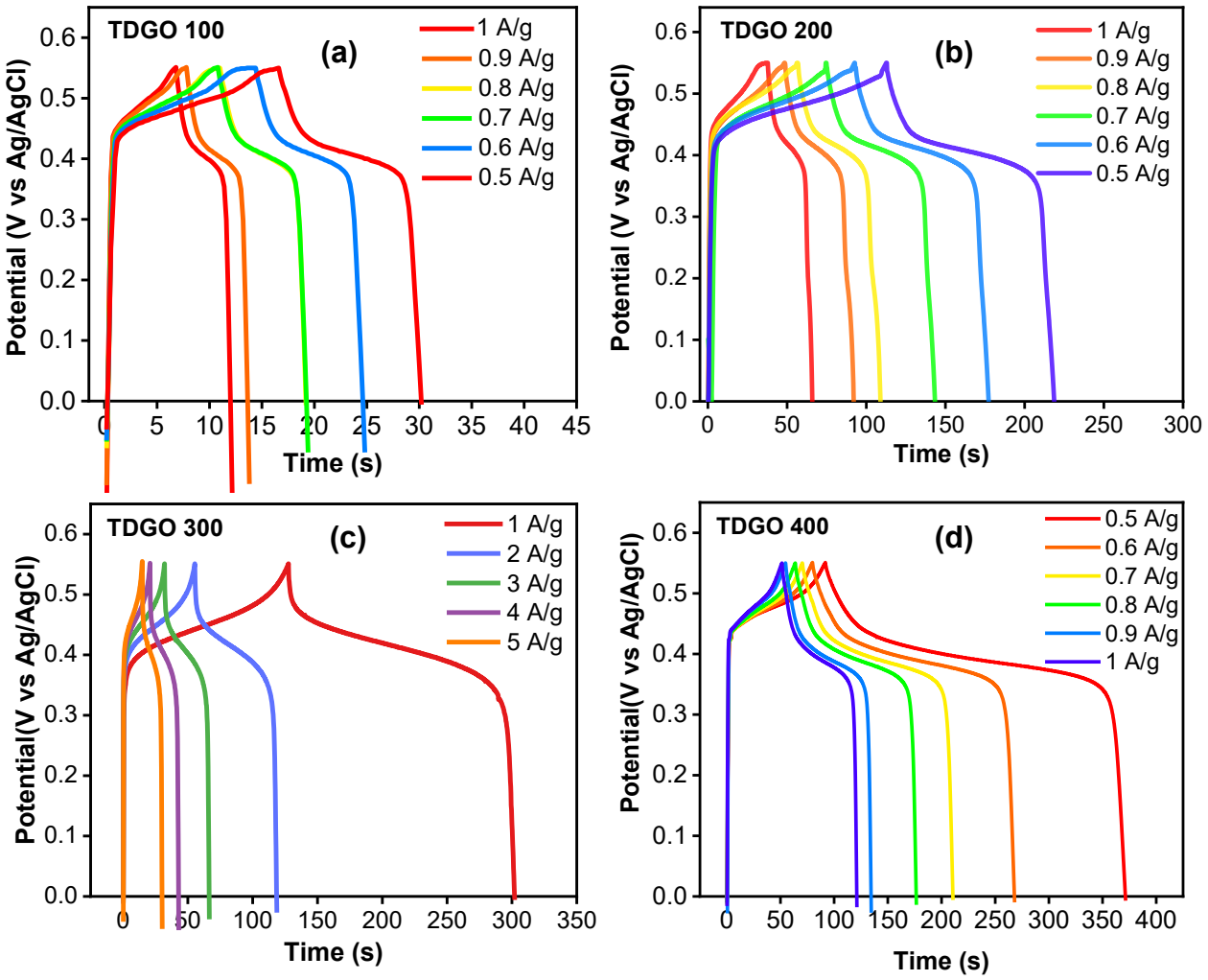

Fig. S7 Galvanostatic charge discharge curves (GCD) of (a) TDGO100, (b) TDGO200, (c) TDGO00, (d) TDGO400 active materials based supercapacitors in three electrode configuration.

Table S2 Energy density power density calculations of TDGO300 in 6 M KOH electrolyte system in three electrode configuration.

Current density (A/g)	Charging Time (s)	Discharge time (s)	Area under the curve	Areal capacitance (F/cm^2)	Energy density (E_d)	Power density (P_d)	Coulombic Efficiency (CE)
1	127.6	174.2	22.5505	316.7	13.3	275	136.5
2	55.4	63	8.6922	229.1	9.62	550	113.7
3	32.1	34.	4.6288	185.4	7.79	825	105.9
4	20.8	22	3.0324	160	6.72	1100	105.7
5	14.8	15.2	1.9936	138.1	5.81	1375	102.7

Optimization of redox additive

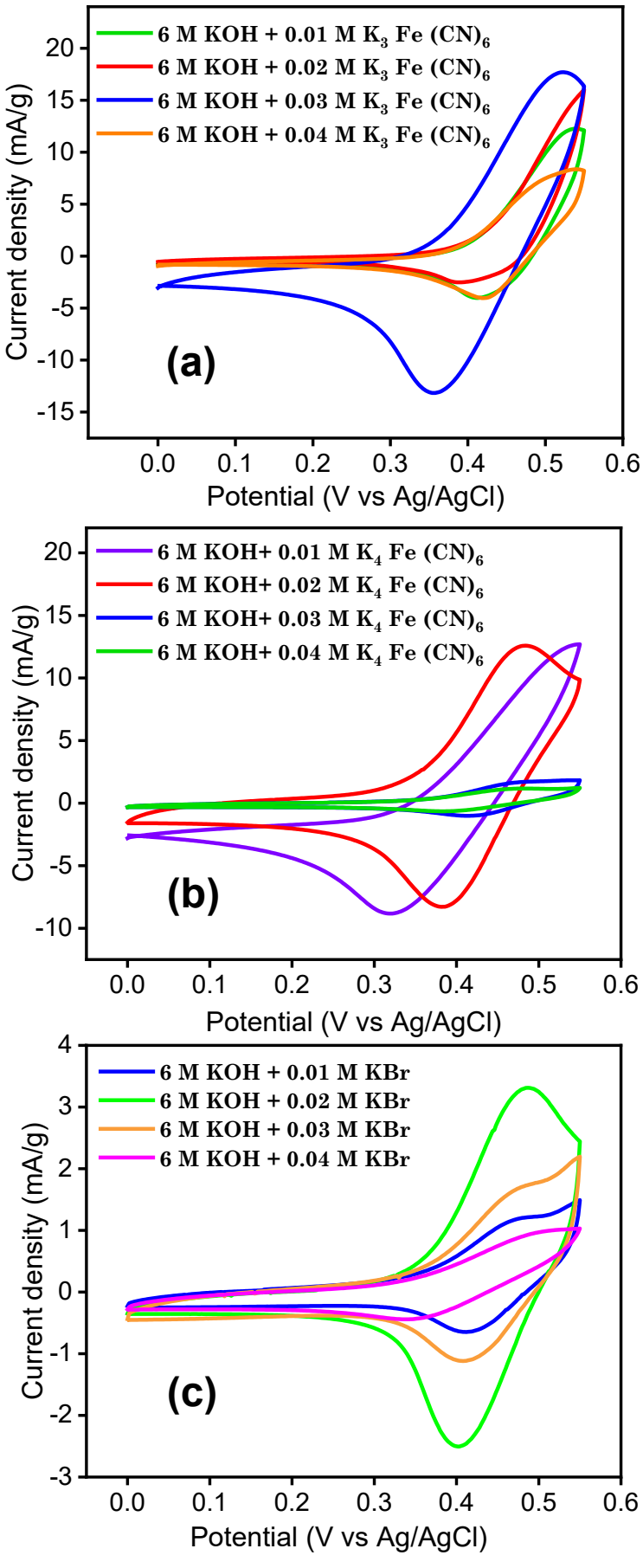

Fig. S8 Cyclic voltammogram of TDGO300 in 6 M KOH with different concentrations of (a) $K_3Fe(CN)_6$, (b) $K_4Fe(CN)_6$, (c) KBr

Table S3 Energy density power density calculations of TDGO300 in (KOH/$K_3Fe(CN)_6$) redox additive electrolyte system in three electrode configuration.

Current density (A/g)	Charging Time (s)	Discharge time (s)	Area under the curve	Areal Specific Capacitance (F/cm^2)	Energy density (E_d)	Power density (P_d)	Coulombic Efficiency (CE)
1	688.2	653.4	98.8943	817.3	34.3	189.2	105.3
2	277.6	278	44.308	732.3	30.7	398.4	99.8
3	163.4	163.6	27.4353	680.2	28.6	628.8	99.8
4	106.6	106.6	18.1942	601.4	25.3	853.4	100
5	75.8	75.6	13.6542	564.2	23.7	1128.8	100.2

Table S4 Energy density power density calculations of TDGO300 in (KOH/K3Fe(CN)6) redox additive electrolyte system in two electrode configuration.

Current density (A/g)	Charging Time (s)	Discharge time (s)	Area under the curve	Areal capacitance (F/cm^2)	Energy density (E_d)	Power density (P_d)	Coulombic Efficiency (CE)
1	289.4	266	49.23	414.6	17.4	235	91.9
2	219.4	171.8	19.67	331.4	13.9	291	78.3
3	121.1	90.9	10.06	254.4	10.6	423	75.1
4	23.2	19.2	5.991	168.1	7.14	1590	105.7