Supplementary Information

Graphene Oxide and Starch Gel as a Hybrid Binder for Environmentally Friendly High-Performance Supercapacitors

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### Supplementary Tables

**Supplementary Table 1.** Slurry composition of different GO-StC and reference electrodes.

| Slurry name | AC (wt%) | CB (wt%) | St (wt%) | GO (wt%) |
|-------------|----------|----------|----------|----------|
| StC         | 85       | 5        | 10.00    | 0        |
| GO-StC-I    | 85       | 5        | 7.50     | 2.50     |
| GO-StC-II   | 85       | 5        | 6.67     | 3.33     |
| GO-StC-III  | 85       | 5        | 5.00     | 5.00     |
| GO-StC-IV   | 85       | 5        | 3.33     | 6.67     |
| GO-StC-V    | 85       | 5        | 2.50     | 7.50     |
| GO-C        | 85       | 5        | 0        | 10       |
Supplementary Table 2. Main peaks positions and calculated structural parameters from XRD patterns of GO-StC, StC, AC, GO, GO-St-gel, GO-St, and St (Fig. 2a of the manuscript). \( d \), \( B \) and \( L_a \) are interplanar spacing in crystal lattice, line broadening at half-maximum intensity of the peak and crystallite lateral size, respectively.

| Sample    | (001) \( 2\theta \) (°) | (002) \( 2\theta \) (°) | (100) \( 2\theta \) (°) | (10) \( 2\theta \) (°) | \( d_{(001) \text{ or } (002)} \) (Å) | \( B_{(100) \text{ or } (10)} \) (°) | \( L_a \) (Å) |
|-----------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------------|---------------------------------|----------|
| GO-StC    | \( \backslash \)         | 21.89                    | \( \backslash \)        | 43.73                    | 4.03                            | 4.66                            | 37.6     |
| StC       | \( \backslash \)         | 22.24                    | \( \backslash \)        | 43.49                    | 3.99                            | 4.07                            | 43.0     |
| AC        | \( \backslash \)         | 22.13                    | \( \backslash \)        | 43.68                    | 4.01                            | 3.93                            | 44.6     |
| GO        | 10.85                    | \( \backslash \)        | 42.57                    | \( \backslash \)        | 8.15                            | 1.36                            | 128.0    |
| GO-St-gel | \( \backslash \)         | \( \backslash \)        | 42.62                    | \( \backslash \)        | \( \backslash \)                | 2.01                            | 86.9     |
| GO-St     | 11.07                    | \( \backslash \)        | 42.50                    | \( \backslash \)        | 7.99                            | 1.59                            | 109.6    |
**Supplementary Table 3.** Main features and relative assignment from FT-IR spectra of GO, GO-St-gel, GO-St, and St (Fig. 2b of the manuscript).

| Code | Wavenumber (cm⁻¹) | GO | GO-St-gel | GO-St | St | Assignment¹, ², ³ |
|------|-------------------|----|-----------|-------|----|------------------|
| 1'   | 3586              | -  | 3586      | -     | -  | \                |
| 1    | 3216              | -  | 3233      | -     | -  | OH stretching    |
| 1    | \                 | 3286         | -       | 3310  | -  | CH₂ bending      |
| 2    | \                 |   | 2931      | -     | -  | \                |
| 3    | \                 |   | 2894      | -     | -  | \                |
| 4    | 1720              | 1726 | 1722      | -     | -  | C=O stretching (Carbonyl) |
| 5    | \                 |   | 1642      | -     | -  | OH bending and stretching of absorbed H₂O |
| 6    | 1615              | 1627 | 1615      | -     | -  | OH bending      |
| 7    | 1373              | 1356 | 1360      | -     | -  | OH bending      |
| 8    | \                 |   | 1241      | -     | -  | C-OH bending    |
| 9    | 1219              | 1230 | 1225      | -     | -  | C-OH stretching |
| 10   | \                 |   | 1207      | -     | -  | CH₂ and C-OH bending |
| 11   | 1165              | -  | -         | -     | -  | C-OH stretching |
| 12   | \                 | 1148 | 1150      | 1150  | -  | C-O/C-C/OH stretching and bending of glycosidic bridge |
| 13   | \                 |   | -         | 1078  | -  | C-OH bending    |
| 14   | \                 |   | -         | 1042  | -  | C-OH bending    |
| 15   | 1038              | -  | 1038      | -     | -  | C-O stretching (Alkoxy) |
| 16   | \                 | 1014 | 1015      | 1016  | -  | C-OH bending    |
| 17   | \                 | 998 | 993       | 995   | -  | C-O-C (Skeletal starch) |
| 18   | 975               | -  | -         | -     | -  | C-O-C stretching (Epoxy) |
Supplementary Table 4. Interbands deconvolution of Raman spectra and resulting $I_D/(I_D+I_G)$ ratio of GO-StC, StC, AC, GO, GO-St-gel, and GO-St. Deconvolution result for GO is shown in Fig. 2d of the manuscript, GO-St-gel and GO-St show similar fittings. Deconvolution result for AC is shown in Fig. 2e of the manuscript, GO-StC and StC show similar fittings. $x_c$, $w$ and $I$ are peak position, full width at half height and peak height, respectively.

| Band   | [Fitting model] | Parameter | Sample         |
|--------|-----------------|-----------|----------------|
|        |                 | GO-StC    | StC            | AC             | GO             | GO-St          | GO-St-gel      |
| $D^*$  | [Gaussian]      | $x_c$ (cm$^{-1}$) | 1231.5         | 1230.5         | 1243.6         |                  |                |
|        |                 | $w$ (cm$^{-1}$)  | \             | 88.7           | 81.9           | 61.8            |                  |
|        |                 | $I$ (counts)     | 874.4          | 943.0          | 1022.6         |                  |                |
| $I$    | [Gaussian]      | $x_c$ (cm$^{-1}$) | 1360.2         | 1350.1         | 1334.9         |                  |                |
|        |                 | $w$ (cm$^{-1}$)  | 234.2          | 251.2          | 324.3          | \               |                |
|        |                 | $I$ (counts)     | 991.7          | 781.7          | 916.1          |                  |                |
| $D$    | [Ps-Voigt]      | $x_c$ (cm$^{-1}$) | 1345.6         | 1345.5         | 1343.9         | 1353.4          | 1354.8         | 1351.0         |
|        |                 | $w$ (cm$^{-1}$)  | 74.8           | 79.1           | 82.1           | 114.1           | 116.0          | 104.8          |
|        |                 | $I$ (counts)     | 2817.5         | 2560.4         | 3252.3         | 19953.7         | 23368.8        | 21706.5        |
| $D''$  | [Gaussian]      | $x_c$ (cm$^{-1}$) | 1557.6         | 1553.0         | 1554.2         | 1508.5          | 1510.0         | 1508.8         |
|        |                 | $w$ (cm$^{-1}$)  | 105.2          | 108.3          | 109.3          | 149.1           | 145.6          | 148.4          |
|        |                 | $I$ (counts)     | 639.2          | 497.8          | 556.0          | 4381.8          | 5313.6         | 4051.0         |
| $G$    | [Ps-Voigt]      | $x_c$ (cm$^{-1}$) | 1607.8         | 1606.8         | 1606.1         | 1587.9          | 1587.6         | 1591.0         |
|        |                 | $w$ (cm$^{-1}$)  | 63.3           | 61.9           | 58.9           | 65.8            | 66.4           | 62.4           |
|        |                 | $I$ (counts)     | 2629.8         | 2322.0         | 2835.5         | 14119.8         | 16627.3        | 13686.1        |
| $D'$   | [Gaussian]      | $x_c$ (cm$^{-1}$) | \             |                |                | 1617.1          | 1617.6         | 1618.4         |
|        |                 | $w$ (cm$^{-1}$)  | \             |                |                | 38.8            | 39.0           | 38.1           |
|        |                 | $I$ (counts)     | 11505.5        | 13023.1        | 12741.6        |                  |                |                |
| $I_D/(I_D+I_G)$ ratio (%) | 51.72 | 52.43 | 53.42 | 58.56 | 58.43 | 61.33 |

\[ \text{V} \]
**Supplementary Table 5.** Starting, ending and peak temperatures of GO reduction and Starch degradation for GO-StC electrode material and GO-St-gel binder compared with reference materials (from TGA and dTGA analysis presented in Figure 3a-b of the manuscript).

| Parameter                        | Sample      | GO-StC | StC | AC | GO   | GO-St-gel | GO-St | St  |
|----------------------------------|-------------|--------|-----|----|------|-----------|-------|-----|
| Reduction start (°C)             |             |        |     |    | 132  | 150       | 122   | 121 |
| Reduction end (°C)               |             |        |     |    |      | 300       | -     | -   |
| Reduction peak (°C)              |             |        |     |    | 216  | 184       | 161   | 180 |
| Maximum red. rate (% / °C)       |             |        |     |    | 3.5  | 18        | 40    | 15  |
| Degradation start (°C)           |             |        |     |    | ~250| 240       | 250   | 286 | 255 |
| Degradation end (°C)             |             |        |     |    | 418  | 385       | 423   | 421 | 329 |
| Degradation peak (°C)            |             |        |     |    | -    | 320       | 313   | 347 | 293 |
| Maximum deg. rate (%/°C)         |             |        |     |    | ~1.2 | 2.8       | 6.7   | 3.9 | 125.2 |

- GO-StC: Graphene oxide-Stearic acid composite
- StC: Starch composite
- AC: Activated carbon
- GO: Graphene oxide
- GO-St-gel: Graphene oxide-Stearic acid-gel binder
- GO-St: Graphene oxide-Stearic acid composite
**Supplementary Table 6** Main peaks positions and calculated structural parameters from XRD patterns of GO-StC coatings thermally treated at varying temperatures (Supplementary Fig. 1a). $d$, $B$ and $L_a$ are interplanar spacing in crystal lattice, line broadening at half-maximum intensity of the peak and crystallite lateral size, respectively.

| Treatment temperature (°C) | (002) $2\theta$ (°) | (10) $2\theta$ (°) | $d_{(002)}$ (Å) | $B_{(10)}$ (°) | $L_a$ (Å) |
|---------------------------|---------------------|-------------------|-----------------|----------------|-----------|
| 80                        | 21.89               | 43.73             | 4.06            | 4.66           | 37.6      |
| 150                       | 22.17               | 43.86             | 4.01            | 3.88           | 45.1      |
| 250                       | 21.72               | 43.52             | 4.09            | 4.63           | 37.8      |
| 350                       | 21.84               | 43.72             | 4.07            | 4.52           | 38.7      |
| 450                       | 21.67               | 43.88             | 4.10            | 5.27           | 33.2      |
| 550                       | 22.24               | 43.66             | 3.99            | 3.81           | 45.9      |
**Supplementary Table 7.** Interbands deconvolution of Raman spectra and resulting $I_D/(I_D+I_G)$ ratio of GO-StC coatings thermally treated at varying temperatures (Supplementary Fig. 1c). $x_c$, $w$ and $I$ are peak position, full width at half height and peak height, respectively.

| Band [Fitting model] | Parameter | Treatment temperature (°C) | 80 | 150 | 250 | 350 | 450 | 550 |
|----------------------|-----------|----------------------------|----|-----|-----|-----|-----|-----|
|                      | $x_c$ (cm$^{-1}$) | | 1360.2 | 1343.6 | 1350.4 | 1365.0 | 1343.6 | 1342.9 |
| $I$ [Gaussian]       | $w$ (cm$^{-1}$) | | 234.2 | 224.3 | 222.6 | 264.2 | 237.1 | 250.6 |
|                      | $I$ (counts) | | 991.7 | 967.8 | 630.9 | 1185.4 | 947.1 | 1052.3 |
|                      | $x_c$ (cm$^{-1}$) | | 1345.6 | 1345.2 | 1344.7 | 1346.3 | 1344.7 | 1344.3 |
| $D$ [Ps-Voigt]       | $w$ (cm$^{-1}$) | | 74.8 | 78.7 | 74.4 | 88.1 | 76.1 | 80.7 |
|                      | $I$ (counts) | | 2817.5 | 3156.9 | 2273.8 | 2216.0 | 3023.5 | 2980.2 |
|                      | $x_c$ (cm$^{-1}$) | | 1557.6 | 1539.2 | 1547.1 | 1552.4 | 1551.5 | 1544.7 |
| $D''$ [Gaussian]     | $w$ (cm$^{-1}$) | | 105.2 | 100.4 | 112.7 | 114.0 | 111.6 | 107.3 |
|                      | $I$ (counts) | | 639.2 | 783.1 | 440.5 | 949.1 | 610.5 | 597.6 |
|                      | $x_c$ (cm$^{-1}$) | | 1607.8 | 1606.5 | 1606.8 | 1606.8 | 1606.1 | 1606.4 |
| $G$ [Ps-Voigt]       | $w$ (cm$^{-1}$) | | 63.3 | 58.7 | 61.8 | 64.3 | 59.9 | 60.2 |
|                      | $I$ (counts) | | 2629.8 | 3164.4 | 2014.8 | 2778.5 | 2713.9 | 3150.1 |
| $I_D/(I_D+I_G)$ ratio (%) | | | 51.72% | 49.94% | 53.02% | 44.37% | 52.70% | 48.61% |
Supplementary Table 8. Electrodes coating specifications (mass loading, $m_l$; thickness, $h$; density, $\rho$) and resulting specific and volumetric capacitance ($C$ and $C_v$, respectively; calculated at 0.2 A g$^{-1}$).

| Electrode      | $m_l$ (mg cm$^{-2}$) | $h$ (µm) | $\rho$ (g cm$^{-3}$) | $C$ (F g$^{-1}$) | $C_v$ (F cm$^{-3}$) |
|----------------|----------------------|-----------|----------------------|------------------|---------------------|
| StC@80         | 2.94                 | 117.52    | 0.25                 | 105.9            | 26.5                |
| GO-StC@80      | 2.81                 | 114.17    | 0.25                 | 125.0            | 30.7                |
| rGO-StC@350    | 2.80                 | 114.56    | 0.22                 | 173.8            | 38.2                |
**Supplementary Table 9.** Fitted values of the simplified equivalent circuit model (Supplementary Fig. 4b) and capacitor properties extrapolated from experimental data for StC@80, GO-StC@80, and rGO-StC@350 supercapacitor symmetric cells.

| Parameter | Supercapacitor symmetric cell | StC@80 | GO-StC@80 | rGO-StC@350 |
|-----------|--------------------------------|--------|-----------|-------------|
| $R_s$ [Ω] |                                | 6.83   | 4.43      | 4.12        |
| $C_{int-T}$ [s^{-1} Ω^{-1}] |                          | 0.02   | 0.01      | 0.01        |
| $C_{int-P}$ |                             | 0.59   | 0.45      | 0.45        |
| $R_{ct}$ [Ω] |                           | 0.29   | 0.78      | 0.70        |
| $W_R$ [Ω] |                                | 4.45   | 8.24      | 3.25        |
| $W_T$ [s] |                                 | 1.62   | 3.01      | 0.33        |
| $W_P$ |                                      | 0.62   | 0.53      | 0.47        |
| $C_{dl-T}$ [s^{-1} Ω^{-1}] |                         | 0.08   | 0.13      | 0.27        |
| $C_{dl-P}$ |                                 | 0.61   | 0.83      | 1.00        |
| $C'$ at 0.01 Hz [F g^{-1}] |                             | 84.6   | 93.9      | 118.5       |
| Phase angle at 0.01 Hz [°] |                               | -72.9  | -77.2     | -77.1       |
| Mid frequency transition [Hz] |                            | 0.32   | 0.32      | 6.31        |
| Response frequency at −45° [Hz] |                         | 0.14   | 0.21      | 0.31        |
| Relaxation frequency [Hz] |                                | 0.05   | 0.13      | 0.32        |
Supplementary Table 10. Comparison of specific capacitance and capacitance retention for different supercapacitors obtained using alternative green binder processable in water and conventional binders of commercially available devices. Some non-biomaterial based alternatives have also been included as reference. Water is used as the only solvent unless differently specified between brackets.

| **Binder** | **Electrolyte** | **Potential window** | **Specific capacitance** | **Capacitance retention** | **Ref.*** |
|------------|-----------------|----------------------|--------------------------|---------------------------|----------|
| rGO-St-gel (350 °C) | PVA/H₃PO₄ gel (60 wt%) | 0−1 V | 174 F g⁻¹ at 0.2 A g⁻¹ | 93.1% [97.1%] after 17,000 [5,000] cycles at 4 A g⁻¹ | This work |
| GO-St-gel (80 °C) | PVA/H₃PO₄ gel (60 wt%) | 0−1 V | 125 F g⁻¹ at 0.2 A g⁻¹ | 92.5% after 5,000 cycles at 4 A g⁻¹ | This work |
| St only (80 °C) | PVA/H₃PO₄ gel (60 wt%) | 0−1 V | 106 F g⁻¹ at 0.2 A g⁻¹ | 92% after 5,000 cycles at 4 A g⁻¹ | This work |
| Potato Starch | 1 M Et₄NBF₄ in PC | 0−1 V | 54 F g⁻¹ at ~0.5 A g⁻¹ | 97.2% after 5,000 cycles at ~1 A g⁻¹ | 15 |
| CMC | 1 M Et₄NBF₄ in PC | 0−5 V | 44 F g⁻¹ at ~0.7 A g⁻¹ | 97.4% after 5,000 cycles at ~1.5 A g⁻¹ | 15 |
| Potato Starch/Guar Gum | 1 M TEABF₄ in PC | 0−2.5 V | 26 F g⁻¹ at 0.2 A g⁻¹ | \ | 18 |
| Starch glue | 1 M TEABF₄ in ACN | 0−2.5 V | ~30 F g⁻¹ at 0.5 A g⁻¹ | ~90% after 2,000 cycles at 0.5 A g⁻¹ | 14 |
| Tragacanth Gum | 1 M TEABF₄ in PC | 0−2.75 V | 23 F g⁻¹ at 1 A g⁻¹ | 97% after 15,000 cycles at ~2 A g⁻¹ | 69 |
| PVAc/poly(isoprene) [Xylene] | 1 M Na₂SO₄ in H₂O | 0−1 V | 41 F g⁻¹ at ~0.1 A g⁻¹ | \ | 68 |
| PVA/PVAc (crosslinked with Na₂B₄O₇) | 1 M Na₂SO₄ in H₂O | 0−1 V | 64 F g⁻¹ at ~0.1 A g⁻¹ | \ | 68 |
| Egg white | 1 M Na₂SO₄ in H₂O | 0−1 V | 89 F g⁻¹ at ~0.1 A g⁻¹ | \ | 68 |
| PTFE [Ethanol] | 1 M Na₂SO₄ in H₂O | 0−1 V | 106 F g⁻¹ at ~0.1 A g⁻¹ | \ | 68 |
| SBR/PTFE | 1 M TEABF₄ in ACN | 0−2.7 V | 108 F g⁻¹ at 0.2 A g⁻¹ | ~80% after 20,000 cycles at ~1 A g⁻¹ | 65-70 |
| PVP [Ethanol] | 1 M TEABF₄ in PC | 0−2.7 V | 112 F g⁻¹ at 0.1 A g⁻¹ | ~81% after 10,000 cycles at 1 A g⁻¹ | 66-72 |
| PTFE [NMP] | 1 M TEABF₄ in PC | 0−2.7 V | 107 F g⁻¹ at 0.1 A g⁻¹ | ~81% after 10,000 cycles at 1 A g⁻¹ | 66-72 |
| Ch/poly(EG-ran-PG) [1% acetic acid in H₂O] | 1 M H₂SO₄ in H₂O | 0−1 V | 172 F g⁻¹ at 0.5 A g⁻¹ | ~99% after 6,000 cycles at 3.5 A g⁻¹ | 67-71 |

* Main manuscript reference number.
Supplementary Figures

Supplementary Fig. 1 Electronic microscope imaging of GO-StC electrodes. a-b SEM images showing: surface morphology of c GO-StC and d StC coatings (scale bar 20 µm).

Supplementary Fig. 2 Physicochemical characterisation of GO-StC coatings at varying thermal treatment temperatures. a XRD patterns, b FT-IR and c RS spectra.
Supplementary Fig. 3 Electrochemical characterisation of GO-StC electrodes with GO amount varying from 0 (StC) to 7.5%. a, c, e, g, i, k Cyclic Voltammetry Scans (CVs) and b, d, f, h, j, l Galvanostatic Charge Discharge Cycles (GCDs). Same legend applies for all CVs and all GCDs. Variation of m specific capacitance and n Equivalent Series Resistance (ESR) with current density. Same legend applies for both panels.
Supplementary Fig. 4 Electrochemical characterisation of GO-StC electrodes with thermal treatment temperatures varying from 80 to 550 °C. a, c, e, g, i, k Cyclic Voltammetry Scans (CVs) and b, d, f, h, j, l Galvanostatic Charge Discharge Cycles (GCDs). Same legend applies for all CVs and all GCDs. Variation of m specific capacitance and n Equivalent Series Resistance (ESR) with current density. Same legend applies for both panels.
Supplementary Fig. 5 Ragone plot of assembled SCs.
Supplementary Fig. 6 Impedance characterisation of supercapacitors. a Schematic of GO-StC symmetric cell with equivalent circuit elements assignment ($R_{s1-2}$ are resistors accounting for leads, current collectors and interparticle series resistances; $R_{s-el}$ accounts for the electrolyte series resistance; $CPE_{int1-2}$ are constant phase elements accounting for interfacial non-ideal capacitances; $R_{ct1-2}$ account for charge-transfer resistances at interfaces; $W_{o1-2}$ are finite length-open Warburg elements accounting for the transmission-line behaviour of porous materials; $CPE_{dl1-2}$ account for non-ideal double-layer capacitances). b Simplified equivalent circuit for EIS fittings where $R_{s}=R_{s1}+R_{s2}+R_{s-el}$, $CPE_{dl}=(CPE_{dl1}+CPE_{dl2})/2$, $Z(R_{ct}-CPE_{int}-W_{o})=Z(R_{ct1}-CPE_{int1}-W_{o1})+Z(R_{ct2}-CPE_{int2}-W_{o2})$. c-d Bode plots of rGO-StC@350 with dried-only GO-StC and StC electrodes (GO-StC@80 and StC@80) included for comparison. Markers represents the experimental points, while solid lines the modelled behaviour with the simplified equivalent circuit. Capacitors response frequency at a phase angle of -45° are specified. Variation of e Real and f imaginary part of complex capacitance for StC@80, GO-StC@80, and rGO-StC@350. Capacitors relaxation frequency (local maxima of $C''$) are specified.
Supplementary Fig. 7 Flow diagram of rGO-StC electrodes fabrication process.
Supplementary Reference

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