Electronic Supplementary Information

Sulfonated polythiophene-interfaced graphene for water-redispersible graphene powder with high conductivity and electrocatalytic activity

Tuan Sang Tran [a], *Rajkamal Balu* [a], *Liliana de Campo* [b], *Naba Kumar Dutta* [a,]*, *and Namita Roy Choudhury* [a,]*

[a] School of Engineering, RMIT University, Melbourne, VIC 3000, Australia.

[b] Australian Centre for Neutron Scattering, ANSTO, Lucas Heights, NSW 2232, Australia

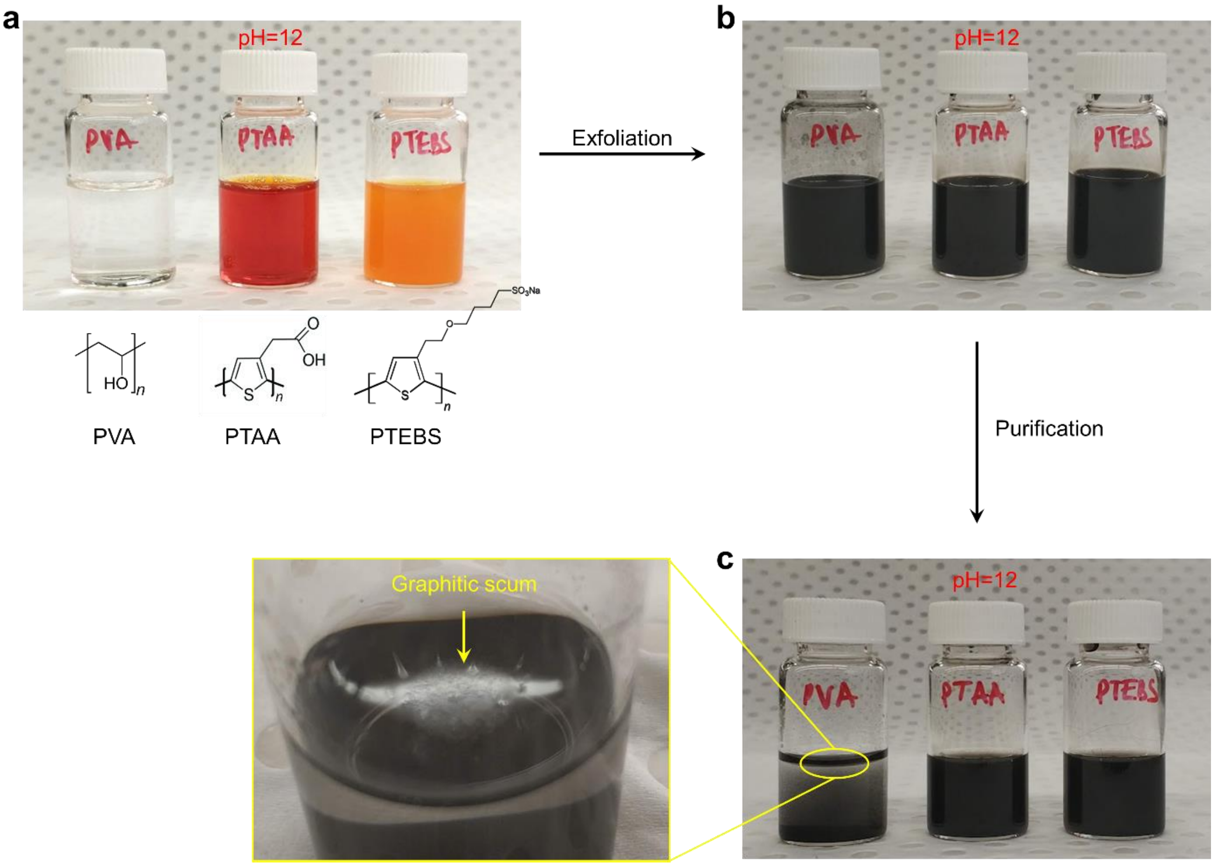
*Corresponding author. Email: naba.dutta@rmit.edu.au; namita.choudhury@rmit.edu.au

Control experiments for exfoliation using diferent stabilisers

Exfoliation using Poly(vinyl alcohol) (PVA): As control experiment, graphene dispersion stabilised by PVA was prepared, where 1 g of graphite was added to 100 mL of PVA solution (10 mg/mL) and sonicated for 120 min. The resulted dispersion was mild-centrifuged at 2000 rpm for 30 min, and the supernatants were collected for purification. To remove PVA from the exfoliated graphene dispersion, the suspension was subjected to two cycles of purification by centrifugation at 20.000 rpm for 60 min to sediment down the graphene flakes and redisperse in deionised water by sonication for 2 min.

Exfoliation using Poly(3-thiophene acetic acid) (PTAA): PTAA is also thiophene-based amphiphilic polymer with very similar chemical structure compared to PTEBS, which consisted of heterocyclic aromatic rings (thiophene groups) appended with acetic acid moieties. However, PTAA is not soluble in pure water, it is only soluble in alkaline solution (pH>12).

First, the liquid medium for exfoliation was prepared by disoving PTAA (10 mg/mL) in alkaline water (pH=12, adjusted using ammonia solution). Then, 1 g of graphite was added to 100 mL of the prepared PTAA solution and sonicated for 120 min. The resulted dispersion was mild-centrifuged at 2000 rpm for 30 min, and the supernatants were collected for purification. To remove the free PTAA from the exfoliated graphene dispersion, the suspension was subjected to two cycles of purification by centrifugation at 20.000 rpm for 60 min to sediment down the exfoliated graphene and redisperse in alkaline water (pH=12) by sonication for 2 min.



Scheme S1: (a) Photograph of the liquid medium (PVA, PTAA, and PTEBS) and their coresponding chemical structures. (b) Comparison of the three graphene dispersions after exfoliation (followed by mild-centrifugation), which are stable black-coloured supernatants, indicating successful exfoliation. (c) Comparison of the PVA-, PTAA-, and PTEBS-exfoliated graphene dispersions after purification to remove the excess stabilisers. While the PTAA- and PTEBS-exfoliated graphene dispersions remain stable without the presence of excessive dispersants, the PVA-exfoliated graphene dispersion is not stable (significant precipitation after 10 min) with the presence of graphitic scum on the surface of water, indicating the aggregation of hydrophobic graphene in water. Moreover, the PTEBS-exfoliated graphene can be dispersed in water whist the PTAA-exfoliated graphene can only dispersed in alkaline solution (pH=12), demonstrating the inextricable relationship between graphene dispersibility and the solubility of the adsorbed polymers.

Control experiments for ORR using different electrodes

For rGO electrode: 20 µL of the rGO dispersion (2 mg mL^{-1}) was spin-coated onto the glassy carbon electrode and then protected with 5 µL of perfluorinated resin solution. The rGO dispersion was prepared by chemical reduction of GO using L-ascorbic acid.[1] Briefly, 100 mL of GO dispersion (0.1 mg mL^{-1}, Sigma Aldrich) was mixed with 100 mg of L-ascorbic acid and heated at 95 °C for 60 min under basic condition (pH ~10, adjusted by ammonia). The resulted rGO dispersion was filtered, washed several times with DI water, and dried in a vacuum oven overnight. Then, 20 mg of the prepared rGO powder was added to 10 mL of aqueous SDS solution (2 mg mL^{-1}) and sonicated for 30 minutes, and used for electrode preparation.

For Pt/C electrode: 10 µL of Pt/C dispersion (1 mg mL^{-1}) was spin-coated onto the glassy carbon electrode and then protected with 5 µL of perfluorinated resin solution. The Pt/C dispersion was prepared according to a well-know recipe in the literature.[2] Briefly, a stock solution of 20% isopropanol and 0.02% Nafion ionomer is prepared by mixing 10 mL of isopropanol with 39.8 mL of deionised water and 0.2 mL of 5 wt% Nafion ionomer solution (Ion Power, Liquion 1100). Then, 10 mg of the Pt/C catalyst (20% Pt on Vulcan carbon) was added to 10 mL of the stock solution and stirred thoroughly for one minute. The mixture was then sonicated for 60 minutes (at 25 °C), and used for electrode preparation.

Calculation of the Electrochemical Surface Area (ECSA) retention

The estimation of the effective active electrochemical surface area (ECSA) of the graphene electrocatalyst was carried out according to the literature:[3]

$$ECSA = \frac{C_{dl}}{C_S} \qquad (1)$$

Where: C_{dl} is the measured double layer capacitance.

C_S is the specific capacitance of the catalyst.

Cyclic voltammetry were performed at various scan rates (10, 20, 50, 100, and 200 mV s^{-1}), and at 200 mV s^{-1} for 10,000 cycles. The double-layer capacitance (C_{dl}) can be determined from the cyclic voltammograms, which is linearly proportional to the ECSA. C_{dl} is estimated by plotting the ΔJ (J_a–J_c) against the scan rate. Since the C_{dl} is proportional to the surface area of the materials, the ratio of the C_{dl} can be regarded as the ratio of the ECSA, proding insign into the durabilily of the G/PTEBS electrocatalysts after 10,000 cycles.

Calculation of the electron transfer number for ORR

For ORR analysis, the CV curve (the background current) in the same voltage range as that of LSV was subtracted from the experimental LSV curve to eliminate any contributions of capacitive current.

On the basis of the RDE data, the electron transfer number per oxygen molecule for ORR can be determined *via* Koutechy-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \qquad (2)$$

Where: J is the measured current density.

J_L is the diffusion-limited current density.

J_K is the kinetic-limited current density.

B is a constant, ω is the electrode rotating rate (rad s^{-1}).

While J_K is assumed to be a constant at a certain potential. J_L is proportional to the square root of angular velocity (ω) of the RDE. The proportionality coefficient (B) is:

$$B = 0.62 n F C_0 (D_0)^{2/3} v^{-1/6} \qquad (3)$$

Where: n is the electron transfer number.

F is the Faraday constant (F = 96485 C mol^{-1}).

C_0 is the saturated O_2 concentration ($C_0 = 1.26 \times 10^{-6}$ mol cm^{-3}).

D_0 is the diffusion coefficient of O_2 ($D_0 = 1.93 \times 10^{-5}$ cm^2 s^{-1}).

v is the kinetic viscosity (v = 0.01009 cm^2 s^{-1}).

The constant 0.62 is adopted when the rotation speed is expressed in (rad s^{-1}). The proportionality coefficient (B) can be determined from the slope of the Koutechy-Levich (K-L) plot based on equation (2). From there, the electron transfer number (n) can be deduced from the slope of the linear plot of J^{-1} versus $\omega^{-1/2}$ (the K-L plot).

Calculation of the printing indicator

The Reynolds number (*Re*) and Weber number (*We*) is calculated according to the following formula:

$$Re = \frac{\rho v r}{\mu} \qquad (4)$$

$$We = \frac{\rho v^2 r}{\sigma} \qquad (5)$$

Where: ρ is the density of the liquid (kg m^{-3}).

v is the velocity of the flow (m s^{-1}).

r is the radius of the tube (m).

μ is the dynamic viscosity (Pa·s).

σ is the surface tension (N m^{-1}).

If the ratio of the Reynolds number to the square root of the Weber number has a value between 1 and 10, then it is likely that ejection of the fluid will be successful.[4] This condition is called the "printing indicator" and is expressed as follow:

$$1 \leq \frac{Re}{We^{1/2}} = \frac{\sqrt{\rho r \sigma}}{\mu} \leq 10 \qquad (6)$$

Calculation of the sheet resistance

The sheet resistance (ohm/square) of graphene films were measured using four-probe method (Kaivo FP-001). The sheet resistance ($R_{\square}$) is calculated according to the following formula:

$$R_{\square} = R_X \times F(D/S) \times F(W/S) \times F_{sp} \qquad (7)$$

Where: R_X is the measured resistance from the tester (Ω).

D is the diameter of the sample (mm).

S is the distance between two neibouring probes (mm).

W is the thickness of the graphene film (mm)

$F(D/S)$ is the diameter corretion factor

$F(W/S)$ is the thickness corretion factor

F_{sp} is the probe distance corretion factor

Table 1: The testing range and current for sheet resistance measurement

Range	Testing range	Resolution	Testing current	Open circuit voltage	Accuracy
200 mΩ	10 μΩ – 200 mΩ	10 μΩ	100 mA	< 5.0 V	± 0.1%
2 Ω	100 μΩ – 2 Ω	100 μΩ	100 mA		
20 Ω	1 mΩ – 20 Ω	1 mΩ	10 mA		
200 Ω	10 mΩ – 200 Ω	10 mΩ	1 mA		
2 kΩ	100 mΩ – 2 kΩ	100 mΩ	100 μA	< 1.0 V	

Table 2: The reference F(D/S) and F(W/S) corretion factor

D/S value	*F(D/S)*	*W/S* value	*F(W/S)*
>200	4.532	<0.4	1.0000
200	4.531	0.4	0.9997
150	4.531	0.5	0.9975
125	4.530	0.6	0.9919
100	4.528	0.7	0.9817
76	4.526	0.8	0.9663
60	4.521	0.9	0.9459
51	4.517	1.0	0.9215
38	4.505	1.5	0.7719
25	4.470	2.0	0.6337
20	4.436	2.5	0.5275
15.4	4.372	3.0	0.4484
12.5	4.294	3.6	0.3780
10	4.171	4.0	0.3420

The resistance testing results were $R_x = 6.6225 \pm 0.005\ \Omega$ (repeated thrice), the size of graphene film (D) is ~20×20 mm, the probe distance (S) is ~1 mm, the thickness (W) is ~30 nm, the probe distance corretion factor $\mathrm{F}_{\mathrm{sp}} = 1.020$, the value of *F(D/S)* and *F(W/S)* can be chosen from the reference Table 2.

$$\begin{aligned} R_{\square} &= R_x \times F(D/S) \times F(W/S) \times F_{sp} \\ &= 6.6225\ (\pm 0.005) \times 4.436 \times 1 \times 1.02 \\ &= 30 \pm 0.002\ \text{(ohm/square)} \end{aligned}$$

Characterisation

UV-visible spectroscopy was performed on a Shimadzu UV-2600. The dispersions were diluted prior to measurement to obtain meaningful absorbance readings. Raman spectrum of graphene powder was recorded using a HORIBA LabRAM HR Evolution with a 532 nm laser excitation. XPS measurement was performed using a Thermo Scientific K-Alpha with a monochromated Al K_α X-ray source. Transmission electron microscopy (TEM) was carried out on a JEOL 2100F TEM. The samples for TEM were prepared by depositing a drop of the graphene dispersions on holey carbon grids and allowed to dry at 60 °C for 24 h in the vacuum oven. Scanning electron microscope (SEM) measurement was carried out on a FEI Nova NanoSEM. The samples were prepared by vacuum filtration of diluted graphene dispersions onto alumina membranes and the films were dried at 60 °C overnight. Atomic force microscopy (AFM) measurement was carried out on a MFP-3D Infinity AFM (Asylum Research). The AFM sample was prepared by drop-casting the dispersion onto an O_2 plasma-treated Si wafer. Rheological measurements were performed on a HR-3 Discovery hybrid rheometer (TA Instruments). Surface tension of the dispersions were measured using a Kruss DSA25 tensiometer. Optical microscope images of the printed patterns was acquired using a Carl Zeiss AxioCam MRc5 Microscope.

Complementary results and discussion

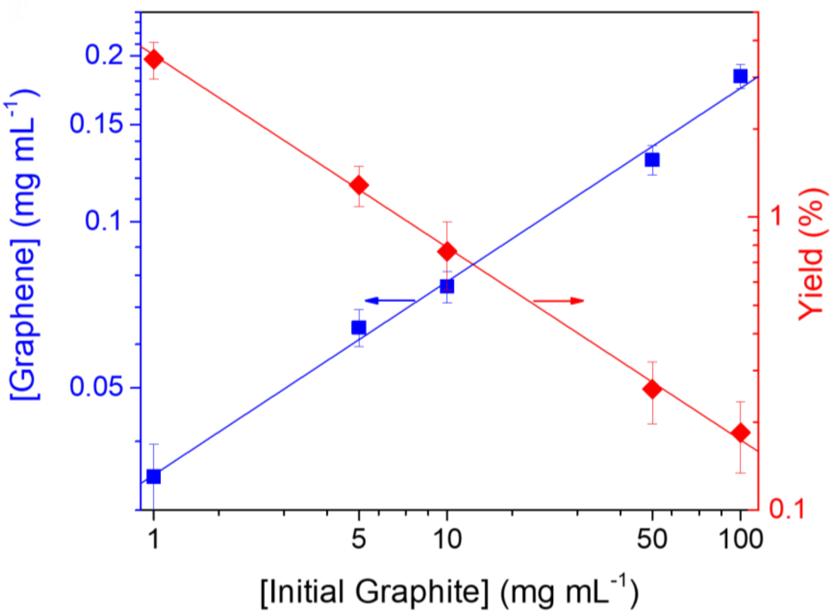


Figure S1: Graphene concentration and yield plotted against the initial graphite concentration. For this set of experiment, the initial PTEBS concentration was set at 1 mg mL^{-1} and sonication time was 1 h. Graphene concentration was measured while controllably varying the initial graphite concentration from 1 mg mL^{-1} to 100 mg mL^{-1}.

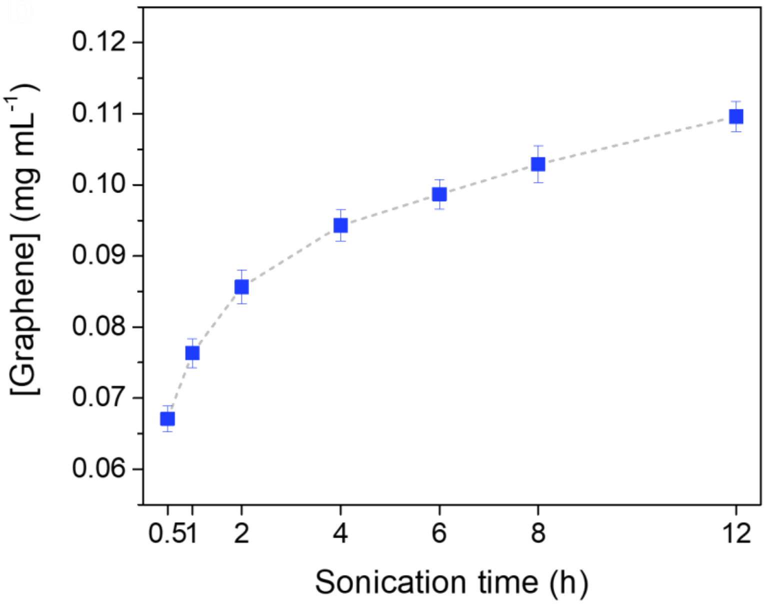


Figure S2: Graphene concentration plotted against sonication time. For this set of experiment, the initial graphite concentration was set at 10 mg mL^{-1} and the initial PTEBS concentration was set at 1 mg mL^{-1}. Graphene concentration was measured by varying the sonication time from 30 min to 12 h.

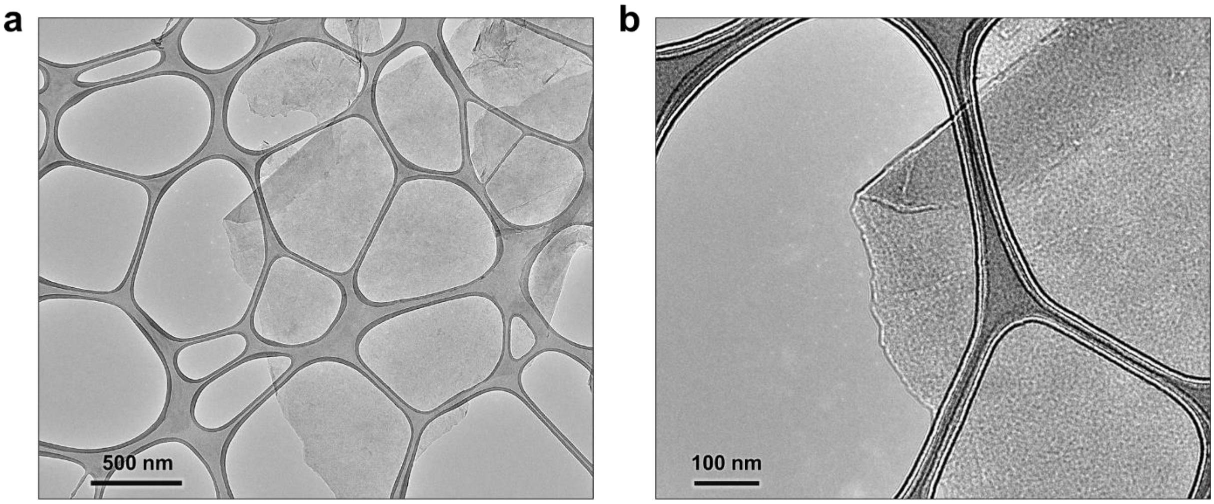


Figure S3: High-resolution TEM images of the exfoliated graphene flakes

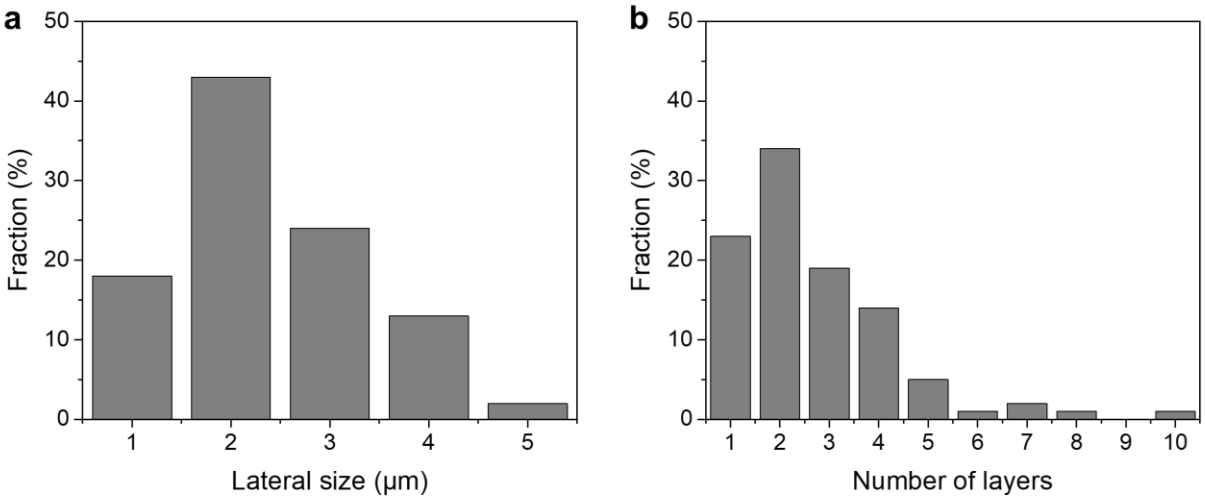


Figure S4: (a) Size distribution and (b) Height distribution of graphene flakes in the dispersion.

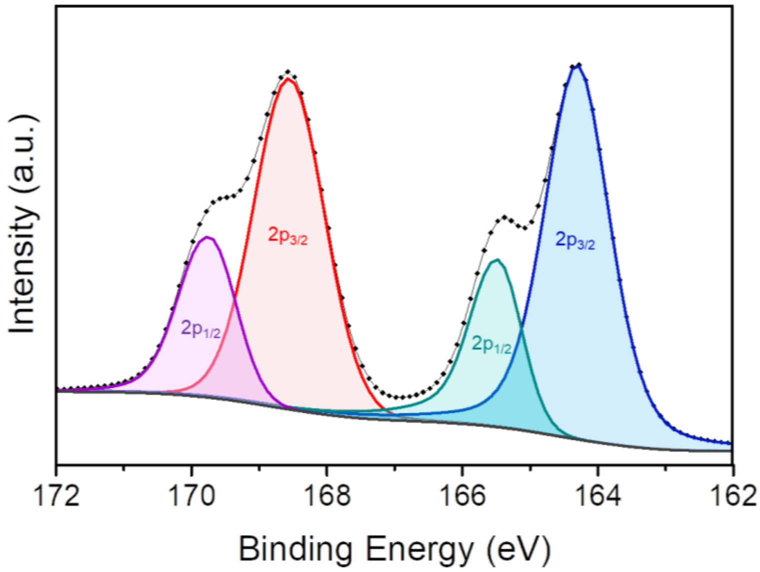


Figure S5: High-resolution S 2p strectra of the PTEBS-interfaced graphene.

Figure S6: Photograph of the graphene powder (left) and the redispersed graphene dispersion (right).

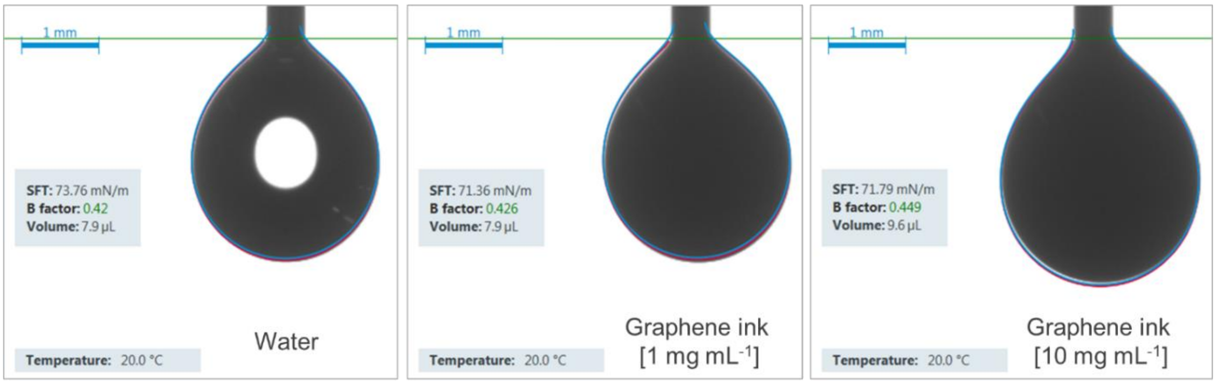


Figure S7: Surface tension of deionised water (left), graphene ink at concentration of 1 mg mL^{-1} (middle), and graphene ink at concentration of 10 mg mL^{-1} (right).

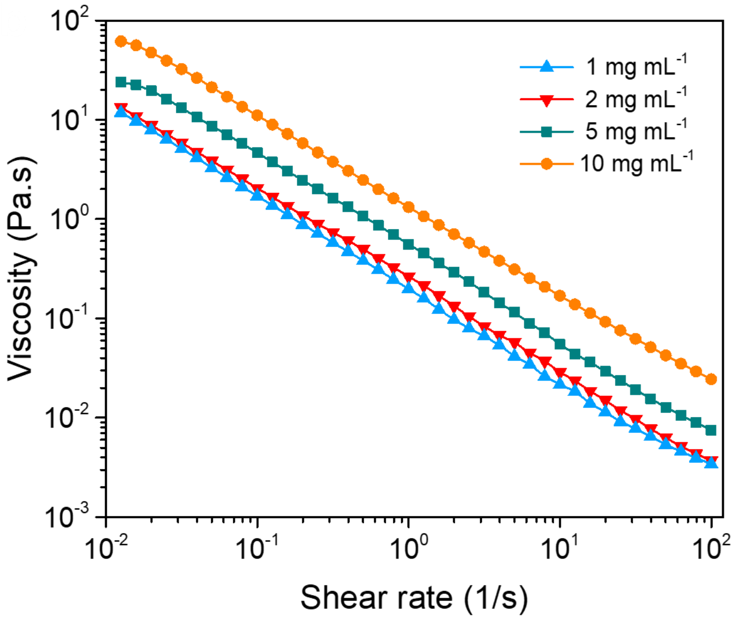


Figure S8: Viscosity of graphene inks at different concentration measured as a function of shear rate.

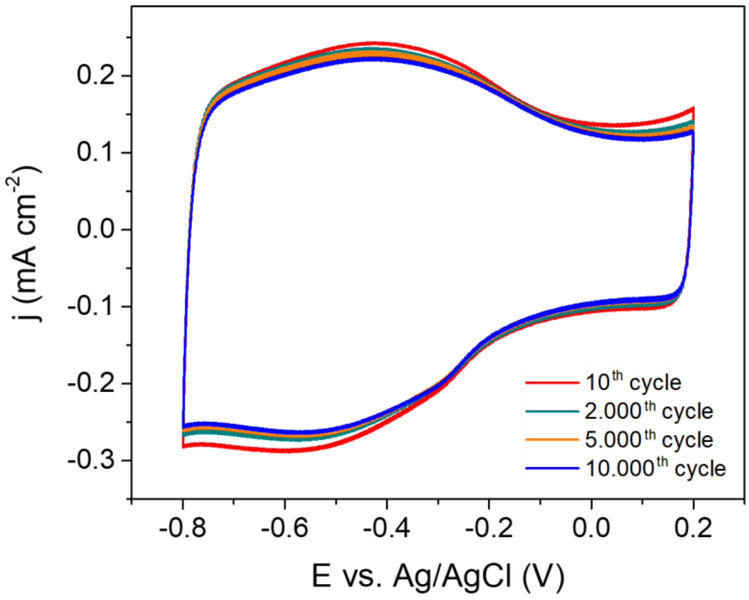


Figure S9: CV curves of the G/PTEBS electrocatalysts after 10,000 cycles measured at scan rate of 200 mV s^{-1}.

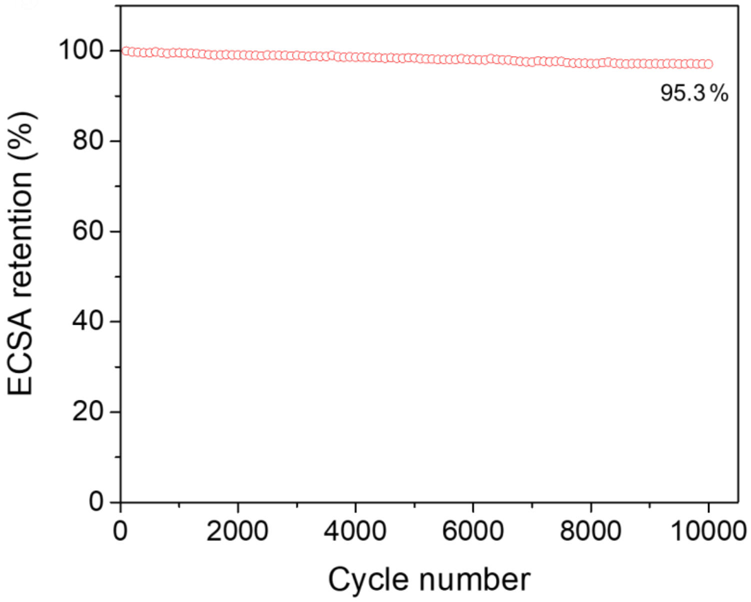


Figure S10: Electrochemical Surface Area (ECSA) retention of the G/PTEBS electrocatalysts after 10,000 cycles.

References

1. Fernández-Merino, M.J., Guardia, L., Paredes, J.I., Villar-Rodil, S., Solís-Fernández, P., Martínez-Alonso, A. and Tascón, J.M.D., Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. *The Journal of Physical Chemistry C*, **2010**, 6426-6432.
2. Garsany, Yannick, Olga A. Baturina, Karen E. Swider-Lyons, and Shyam S. Kocha. "Experimental methods for quantifying the activity of platinum electrocatalysts for the oxygen reduction reaction." *Analytical Chemistry*, **2010**, 6321-6328.
3. Lukowski, Mark A., Andrew S. Daniel, Fei Meng, Audrey Forticaux, Linsen Li, and Song Jin. "Enhanced hydrogen evolution catalysis from chemically exfoliated metallic MoS_2 nanosheets." *Journal of the American Chemical Society*, **2013**, 10274-10277.
4. Gibson, I.; Rosen, D. W.; Stucker, B. Additive manufacturing technologies, Springer, **2014,** Vol. 17.