Supporting Information

Patternable Solvent-Processed Thermoplastic Graphite Electrodes

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Step 1 Electrode Fabrication- Solution Preparation

Small centimeter sized PMMA pieces (Optix, Plaskolite) were massed and placed in a vial, then mixed with dichloroethane typically in a ratio of ~5 mL solvent to 1 gram of PMMA, and kept for a period of months as stock solutions. When using dichloroethane, the small pieces of PMMA dissolved in about 24 hours. Dichloroethane and chloroform were found to be aggressive solvents for dissolving PMMA, and acetone, ethyl acetate, and DMF were also effective solvents. Toluene, xylenes, and propylene carbonate (PC) could dissolve the PMMA, however, the process took longer than a week to fully dissolve. Once fully dissolved, carbon was added and the solvent level was adjusted to achieve a uniform mixture. A consistency of viscous oil was found to be desirable for the solvent/PMMA/carbon mixtures. Before use, the mixture was vortex mixed for ~ 3 min, in a 20 mL scintillator vial. If the mixture was too viscous, efficient mixing did not occur. Sonication was not used in order to avoid altering the chemical structure of the particles or the binder. The resulting mixtures were kept as stock solutions and were seemingly indefinitely stable, and only required remixing by vortex before use.

Step 2 Electrode Fabrication- Templating

To create patterned (templated) electrodes, the oil-like solvent/PMMA/carbon mixture was poured onto silicon wafers, which served as an inert non-stick surface. The solvent loaded electrode mixture was constantly worked with a small wooden stick on the wafer to facilitate solvent evaporation while in a fume hood. Once the material could be formed into a ball of stiff chewing gum-like consistency, then it was firmly pressed into the PMMA template. A CO_2 laser (Epilog Zing) was used to cut and/or etch PMMA electrode templates from stock PMMA sheets(6 or 3 mm thick). The electrode was then placed into a heat press consisting of two brass plates, a piece of PDMS was placed on one side of the electrode. A temperature of ~60 °C with a pressure of ~50 psi was used. If the TPE mixture was too full of solvent, or too high of a temperature or pressure is used, the finished electrode may be deformed or the template may be disfigured. In most cases the electrode was left overnight under pressure and heat. The dried electrode was then sanded with 200 or 300 grit sand paper to remove the excess TPE material, then finished with 600 grit sand paper for a smoother surface. The electrode and the template can be further smoothed by following sanding by polishing with alumina. To finish the electrode, a metallic wire was attached to one side of the TPE using a small amount of silver paint and then covered with two part epoxy. The entire process is shown schematically in Figure 1A in the main text.

Conductivity measurements-

Resistivity (inverse of conductivity) was measured by a two point probe (Fluke 187 multimeter, accuracy of 0.01 Ω) placed on two opposing faces of a TPE cylinder which was made with a PMMA mold. The faces of the cylinder were coated with a thin layer of silver paint to compensate for contact resistance. Typical diameters were 3 to 5 mm. In the cases of very low resistivity, longer cylinder lengths and smaller diameters can be used. The dimensions of the cylinder were adjusted to try to keep measured resistances above 1 Ω to minimize error. It was important to subtract background resistance inherent with a metal to metal contact, which was variable but typically around 0.3 Ω. The background was measured by shorting the silver coated copper pads of the multimeter, which mimicked the silver-silver contact in TPE conductivity measurements. Equation S1 describes conductivity and resistivity, where ρ is resistivity, R (Ω) is resistance, *D* is diameter of disk, *L* is length, and σ (S/m) is conductivity.

$$\rho = R * \frac{\pi(0.5D)^2}{L} \quad \text{and} \quad \sigma = 1/\rho$$

equation S1.

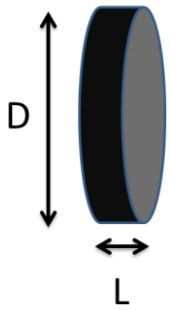

Figure S1. Example of a templated cylinder TPE used for conductivity measurements.

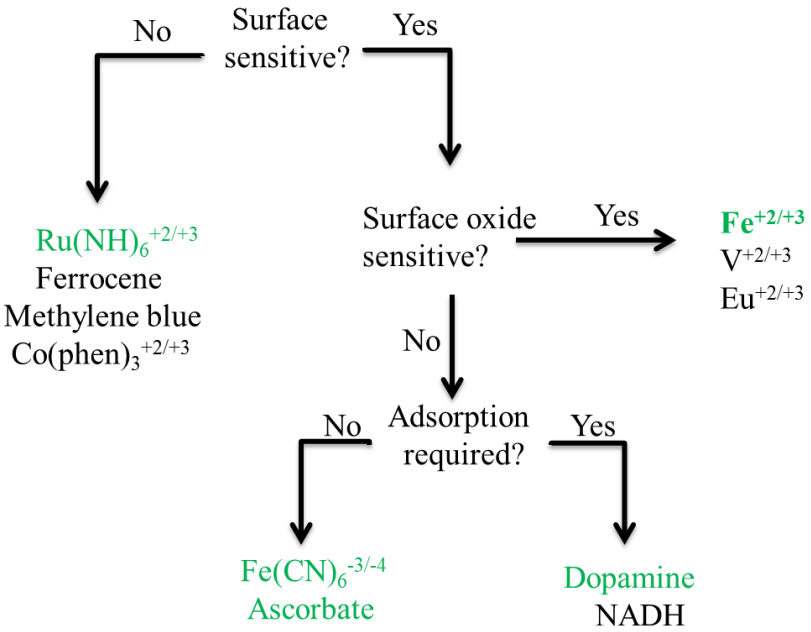

Figure S2. Flow chart for describing electrode surface sensitivity towards various analytes proposed by McCreery. The analytes in green were tested in this work.

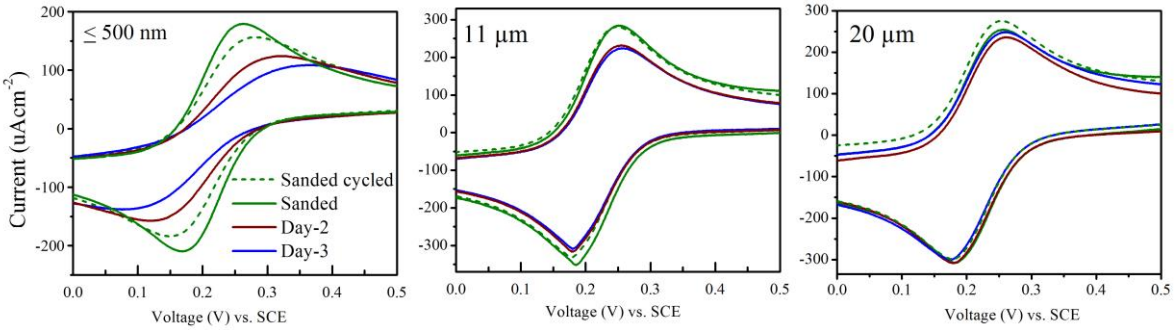

Figure S3. Stability data for a 1:0.55, ≤500 nm TPE, 1:2, 11 µm TPE, and 1:3, 20 µm TPE over the course of 3 days in 0.5 M KCl with 1 mM ferricyanide at 100 mV s^{-1}. The dotted lines are after repeated cycling (25 cycles) in ferricyanide on the first day of testing. The electrodes were left, dry, in ambient atmosphere between trials. Fresh solution was used for each day of testing and minor changes in concentration from day to day may be expected.

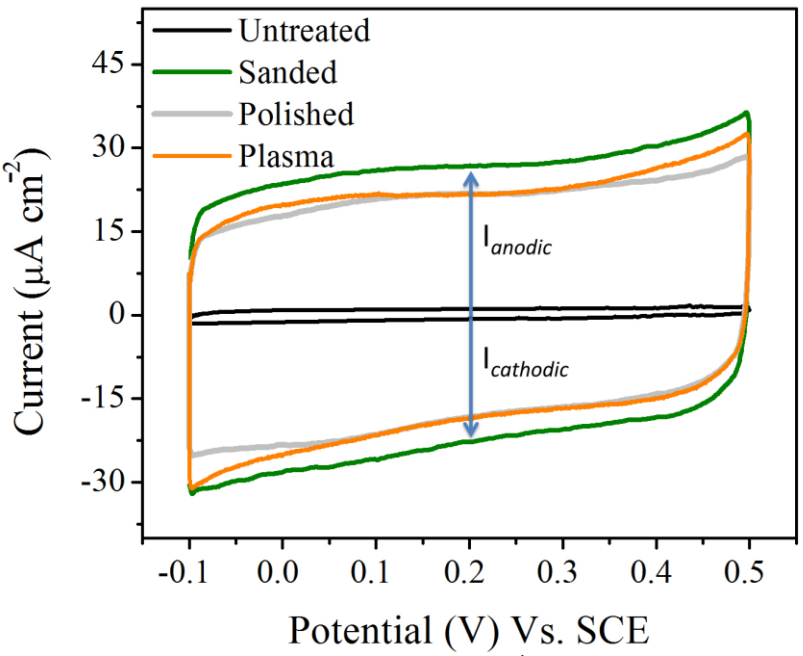

Figure S4. Averaged cyclic voltammograms 100 mV s^{-1} (*n*=3) from the various surface treatments performed on a 1:2, 11 µm TPE. The solution for all capacitance measurements, including the main text, was 0.5 M KCl.

Irreversible peak current calculation-

Were I_P is the peak current, *n* is the number of electrons, α electron transfer coefficient, *A* is area, *C* is concentration, *D* diffusion coefficient, *v* is the scan rate.[1] The electron transfer coefficient used here was 0.5, and the ascorbic acid diffusion coefficient was 6.5E^{-6} cm/s.[2]

$$I_{p=3.01x10^5 n[(1-\alpha)n_a]^{1/2} ACD^{1/2} v^{1/2}}$$ **equation S2.**

Reversible peak current calculation-

Equation S3 is a simplified version of the Randles-Sevcik equation assuming a temperature of 25 ^{0}C. Were I_P is the peak current, *n* is the number of electrons, *A* area, *C* concentration, *D* diffusion coefficient, *v* is the scan rate. Dopamine coefficient of 4.15E^{-6} cm/s taken from previous literature,[3] ferricyanide 6.67E^{-6} cm/s,[4] and hexaammineruthenium(III) chloride 7.9E^{-6} cm/s.[4]

$$I_{p=2.69x10^5 n^{3/2} ACD^{1/2} v^{1/2}}$$ **equation S3.**

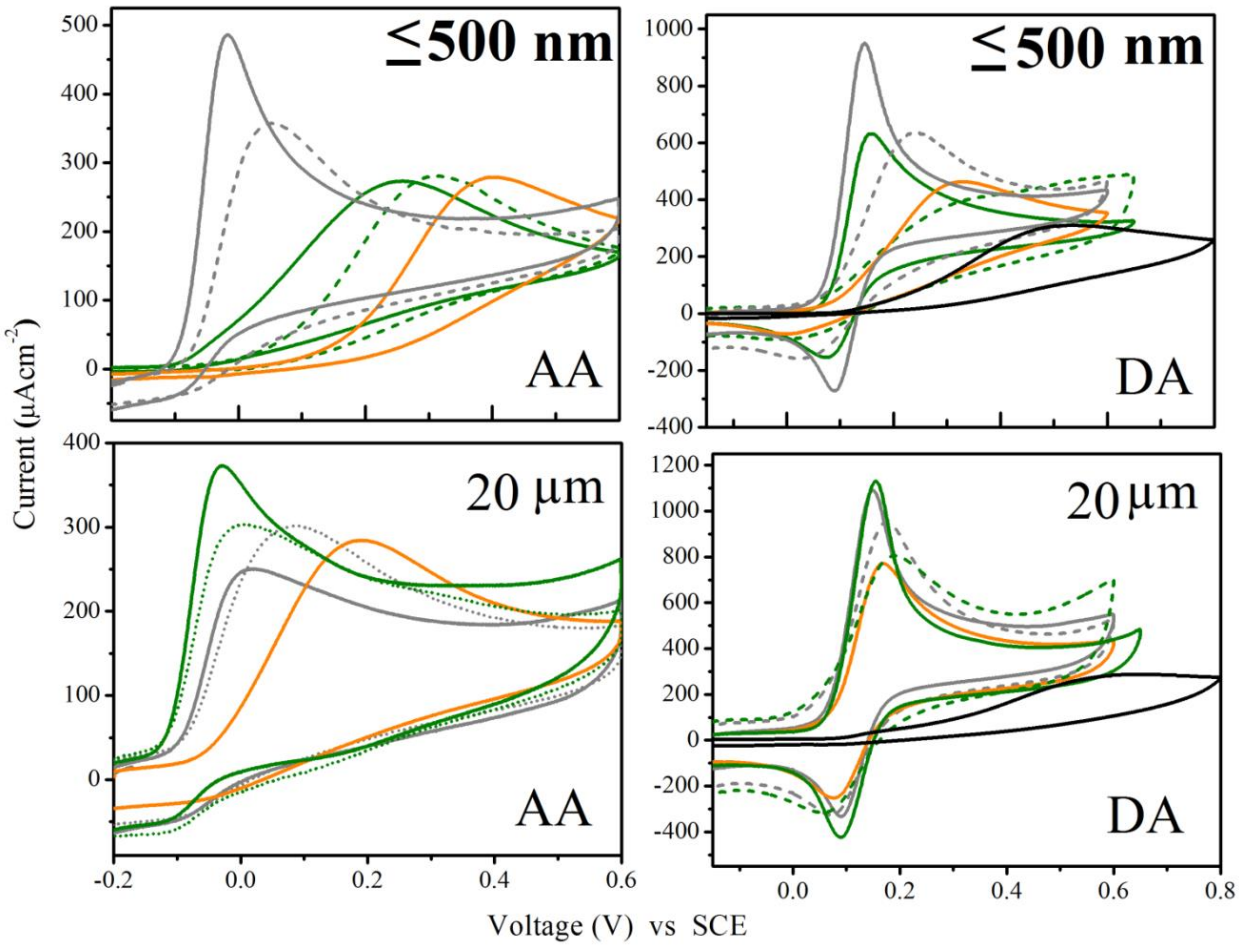

Figure S5. Cyclic voltammograms 100 mV s^{-1} of a 1:0.55, ≤500 nm, and 1:3, 20 µm TPE with 1 mM ascorbic acid (AA), 1 mM dopamine (DA), in 0.1 M phosphate buffer at pH 7.4. Orange = polished, green = sanded, grey = plasma treated, black = untreated. Dashed lines are a cyclic voltammograms after the electrode has been cycled in the respective solution for 25 cycles.

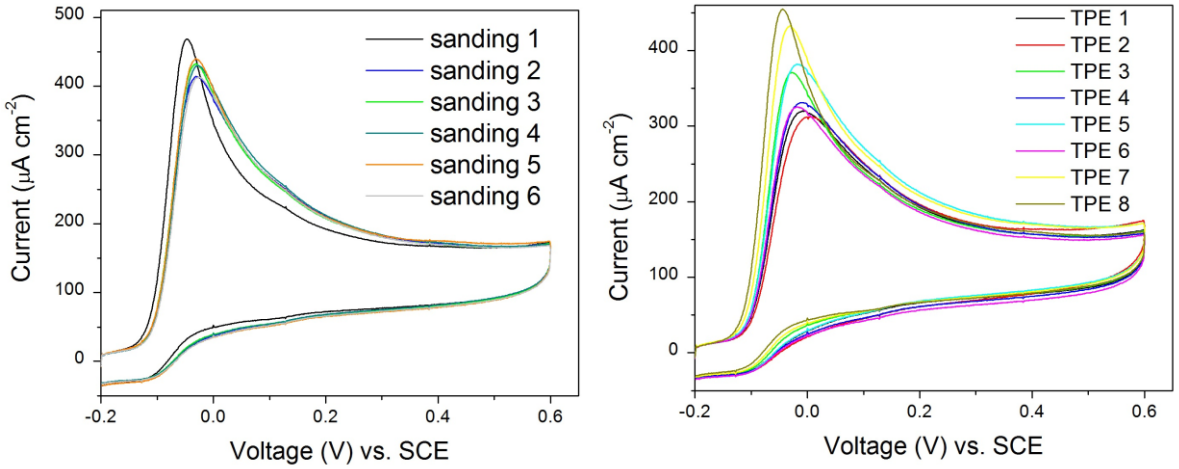

Figure S6. (left) Cyclic voltammetry of 11 µm TPE in a ratio of 1:2 PMMA:carbon with 1 mM AA in phosphate buffer at pH 7.4. (right) Cyclic voltammetry for 8 individual 11 µm TPE in a ratio of 1:2 PMMA:carbon with 1 mM AA in phosphate buffer at pH 7.4. Scan rates for all trials were 100 mV s^{-1}.

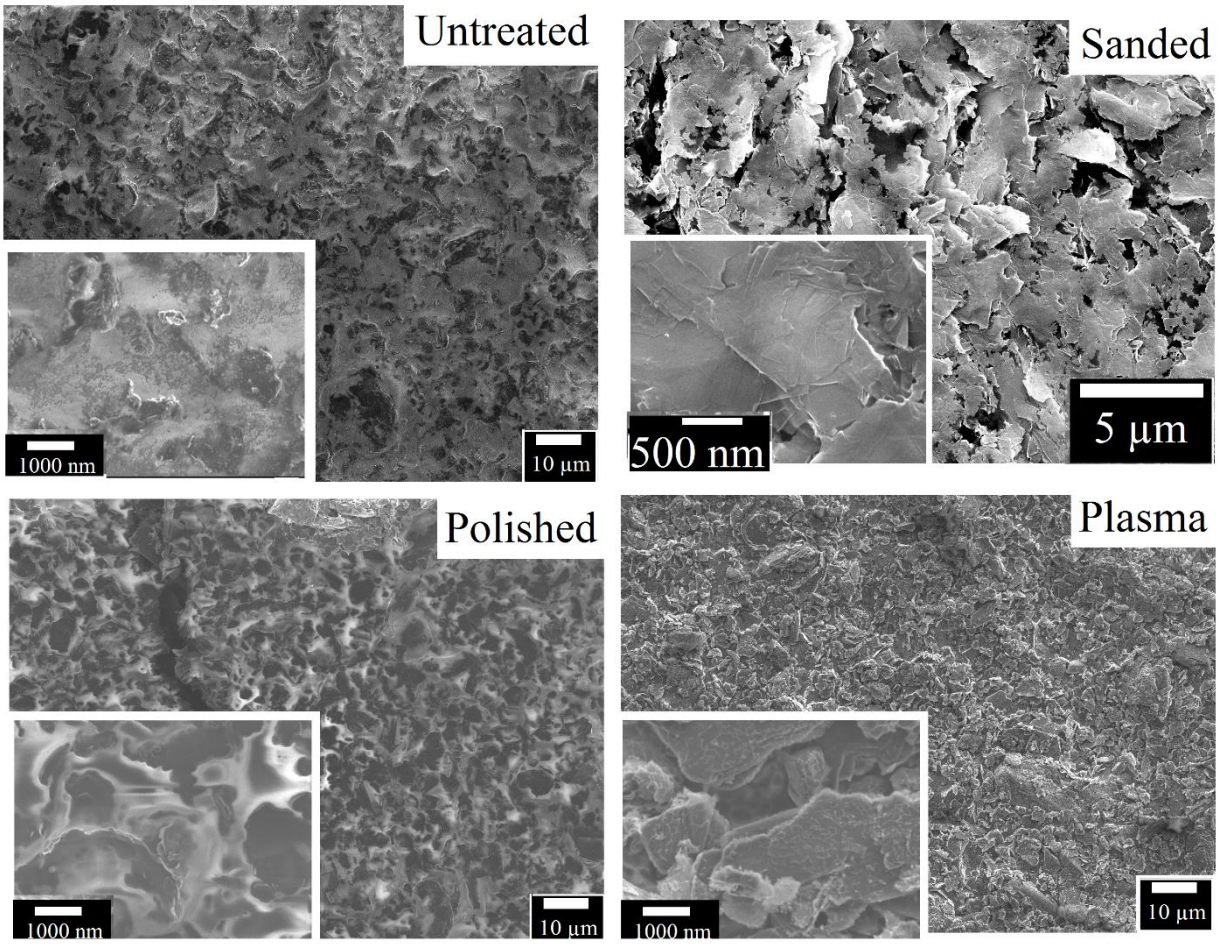

Figure S7. SEM images of a 1:3, 20 µm TPE with various surface treatments.

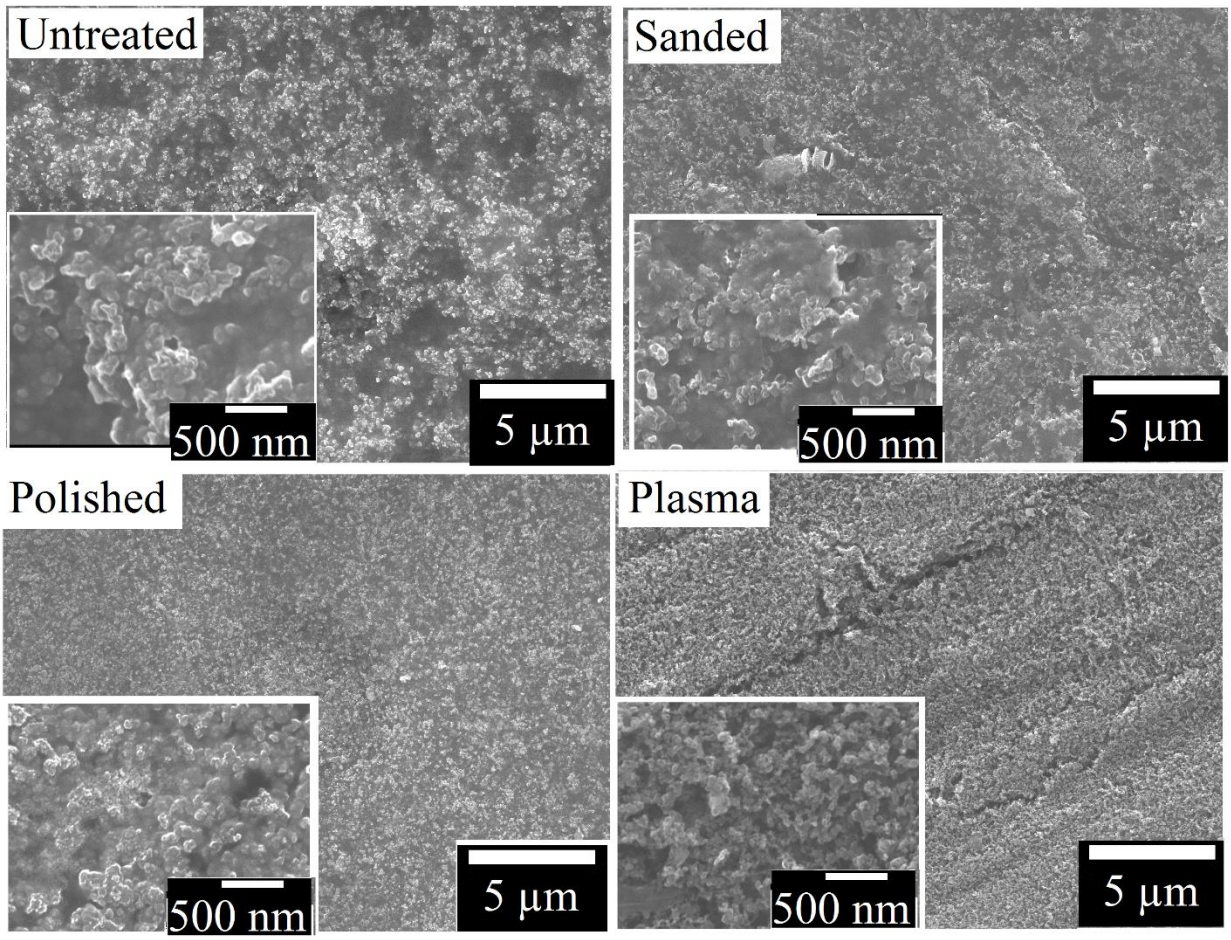

Figure S8. SEM images of a 1:0.55, ≤ 500 nm TPE with various surface treatments.

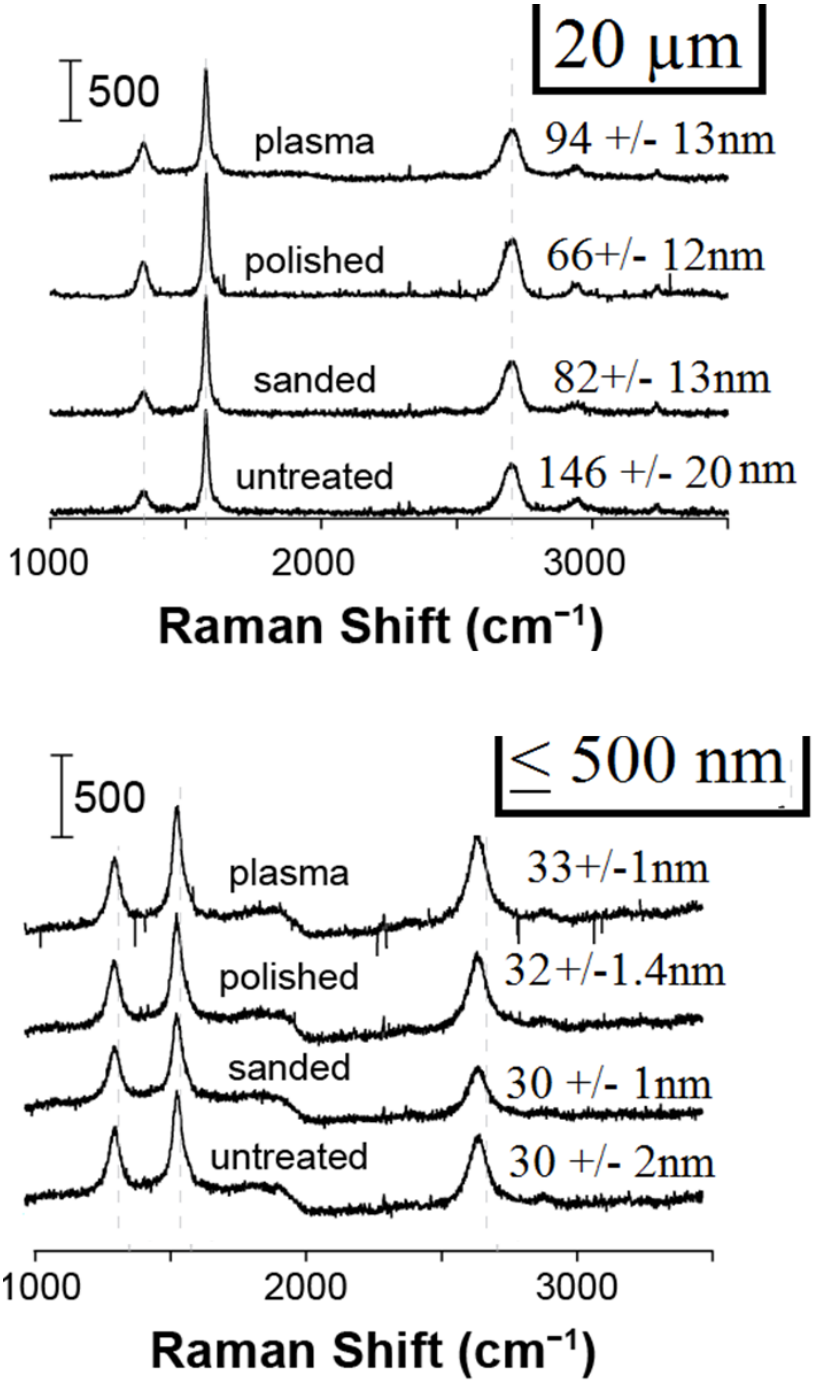

Figure S9. Averaged Raman spectra of a 1:3, 20 µm and 1:0.55, ≤500 nm TPE with various surface treatments. The calculated (eq 2 materials and methods) crystallite domains are above the respective spectra.

***20* µm**	2D' peak location	error	2D' Height	error	2D' Width	error	D+G peak location	error	D+G Height	error	D+G Width	error
untreated	3239.5	2.6	54.0	6.5	23.2	2.8	2941.5	3.4	42.7	4.0	42.7	7.7
sanded	3238.9	2.0	73.4	9.6	14.3	2.1	2941.1	2.8	36.7	8.6	44.1	7.8
polished	3239.7	1.6	89.4	9.2	14.8	1.3	2939.8	1.9	66.1	16.6	45.1	4.5
plasma	3239.2	2.0	79.9	6.2	18.1	2.1	2939.3	2.3	48.9	19.3	45.0	3.9
***20* µm**	2D peak location	error	2D Height	error	2D Width	error	G peak location	error	G Height	error	G Width	error
untreated	2702.8	1.4	386.9	30.4	60.0	1.4	1574.4	1.3	862.8	46.9	18.3	0.6
sanded	2701.7	1.5	532.1	44.7	60.5	1.2	1574.9	0.9	1018.9	55.2	19.7	0.7
polished	2702.2	1.3	519.6	38.6	61.1	1.0	1575.9	0.5	999.8	85.7	19.1	0.7
plasma	2703.2	1.6	470.4	41.6	60.4	1.3	1575.7	1.0	990.2	68.7	18.9	0.5
***20* µm**	D' peak location	error	D' Height	error	D' Width	error	D peak location	error	D Height	error	D Width	error
untreated	1611.4	2.4	24.0	11.0	22.5	3.8	1342.8	1.8	109.7	11.0	36.7	2.1
sanded	1616.0	2.1	50.9	12.0	8.1	3.7	1343.4	1.0	231.2	39.5	35.1	1.4
polished	1616.9	1.5	78.1	14.4	8.6	2.1	1343.0	0.9	287.4	38.7	34.1	1.0
plasma	1615.4	1.5	54.4	6.8	7.3	2.3	1343.2	1.1	203.3	31.8	37.5	1.4

***11* µm**	2D' peak location	error	2D' Height	error	2D' Width	error	D+G peak location	error	D+G Height	error	D+G Width	error
untreated	3238.0	1.7	56.1	8.0	17.7	2.0	2942.6	2.1	81.7	24.6	41.8	4.8
sanded	3238.1	2.0	63.7	8.9	17.3	1.7	2938.9	1.9	47.9	17.0	53.7	8.7
polished	3239.6	2.2	67.9	10.3	15.2	1.3	2941.1	2.7	64.2	14.0	33.9	2.2
plasma	3238.5	1.8	60.1	8.8	13.9	1.7	2939.4	2.0	68.1	23.9	48.3	7.3
***11* µm**	2D peak location		2D Height		2D Width		G peak location		G Height		G Width	
untreated	2701.3	0.6	402.6	23.8	60.1	1.9	1574.5	0.9	821.0	56.1	19.5	0.5
sanded	2701.3	0.9	444.6	31.2	58.8	1.1	1573.6	1.2	979.8	72.0	19.2	0.5
polished	2701.4	1.3	507.1	39.6	59.9	1.0	1574.9	0.8	997.7	108.7	18.9	0.5
plasma	2701.8	1.6	414.4	30.1	61.5	1.8	1574.3	1.6	929.2	58.3	20.0	1.0
***11* µm**	D' peak location	error	D' Height	error	D' Width	error	D peak location	error	D Height	error	D Width	error
untreated	1614.2	1.6	41.4	10.2	8.3	2.4	1344.0	1.4	157.5	12.7	35.0	1.8
sanded	1614.6	1.9	44.1	4.7	5.5	2.5	1342.3	1.8	169.0	19.2	34.3	1.5
polished	1616.9	2.4	67.5	13.6	7.2	2.8	1342.0	1.8	275.2	37.3	32.4	0.6
plasma	1613.6	2.3	61.3	17.9	11.4	3.9	1342.7	1.5	234.7	70.2	35.1	1.4

400 nm	2D' peak location	error	2D' Height	error	2D' Width	error	D+G peak location	error	D+G Height	error	D+G Width	error
untreated	NA		NA		NA		2918.5	1.7	37.3	4.4	40.8	8.6
sanded	NA		NA		NA		2921.1	4.1	17.5	3.5	44.0	13.5
polished	NA		NA		NA		2921.5	3.3	36.6	6.9	53.4	12.0
plasma	NA		NA		NA		2919.5	2.9	38.1	6.0	44.7	7.8
400 nm	2D peak location		2D Height		2D Width		G peak location		G Height		G Width	
untreated	2670.9	1.3	413.1	21.4	70.7	3.1	1562.0	1.0	551.0	32.3	34.8	0.8
sanded	2670.4	1.5	287.0	8.2	75.1	3.8	1561.4	0.8	468.8	11.2	35.5	0.8
polished	2670.0	0.8	425.6	17.5	68.8	1.9	1560.8	0.8	570.6	20.1	35.3	0.7
plasma	2670.5	1.3	513.2	17.1	71.6	3.5	1561.2	0.7	635.2	27.7	34.5	0.9
400 nm	D' peak location	error	D' Height	error	D' Width	error	D peak location	error	D Height	error	D Width	error
untreated	1598.3	1.1	47.0	8.1	17.6	2.6	1330.1	1.1	345.1	12.6	38.7	0.5
sanded	1598.1	0.5	35.4	8.4	14.4	2.4	1330.1	1.3	295.4	9.5	40.6	1.2
polished	1598.2	0.5	35.8	9.4	14.6	3.0	1329.3	0.8	340.5	8.7	38.0	1.1
plasma	1598.1	0.4	43.0	7.8	20.1	2.6	1330.3	1.2	370.1	16.2	39.6	0.3

Table S1. Average and standard deviation from 49 individual Raman spectra of PMMA:carbon of 1:2, 11 µm, 1:3, 20 µm and 1:0.55, $\leq$ 500 nm TPE with various surface treatments.

References-

1. Yu, D.; Wei, L.; Jiang, W.; Wang, H.; Sun, B.; Zhang, Q.; Goh, K.; Si, R.; Chen, Y., *Nanoscale* **2013,** *5*, 3457-3464.
2. Raoof, J.-B.; Ojani, R.; Hosseinzadeh, R.; Ghasemi, V., *Anal. Sci.* **2003,** *19*, 1251-1258.
3. Wang, Q.; Li, N.; Wang, W., *Anal. Sci.* **2002,** *18*, 635-639.
4. Moldenhauer, J.; Meier, M.; Paul, D. W., *J. Electrochem. Soc* **2016,** *163*, 672-678.