nanomaterials

Supporting Information File

Sustainable Preparation of Nanoporous Carbons via Dry Ball Milling: Electrochemical Studies Using Nanocarbon Composite Electrodes and a Deep Eutectic Solvent as Electrolyte

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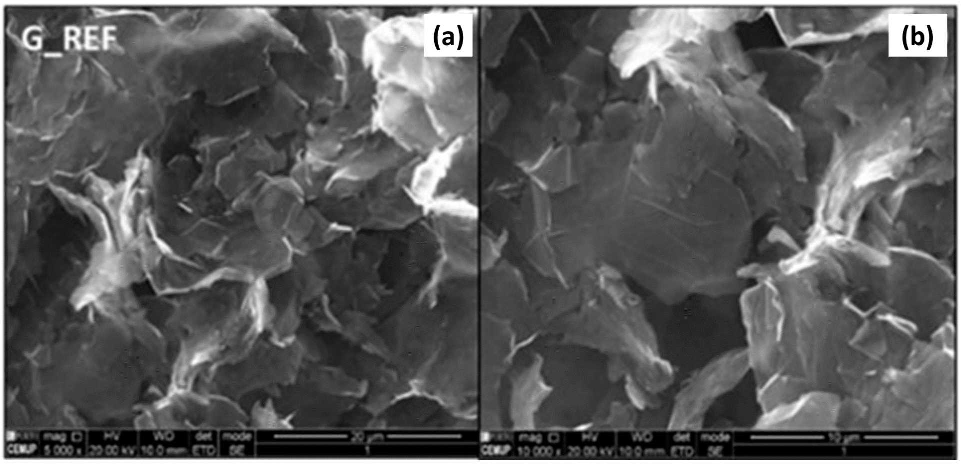
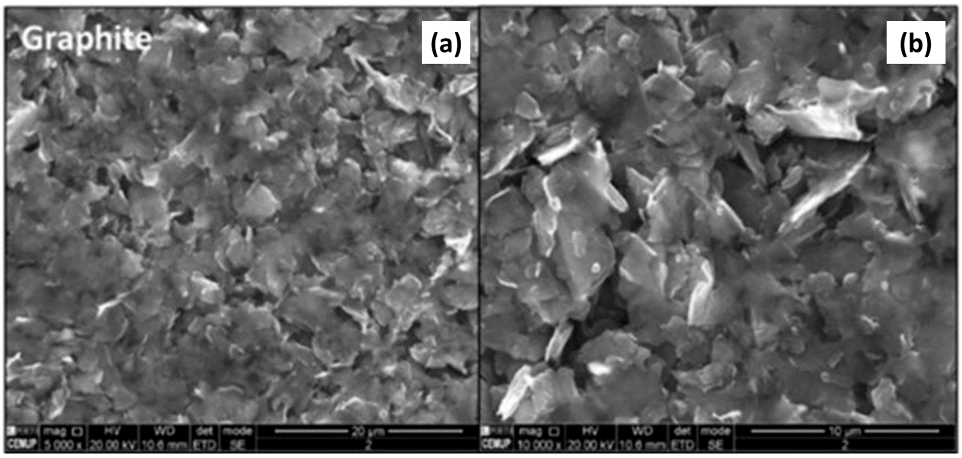
Morphological studies: SEM analysis



(A)



(B)

Figure S1. Electron microscopy images showing the structure of G_REF (**A**) and commercial graphite (**B**) samples with 5000× (a), 10000× (b) magnification.

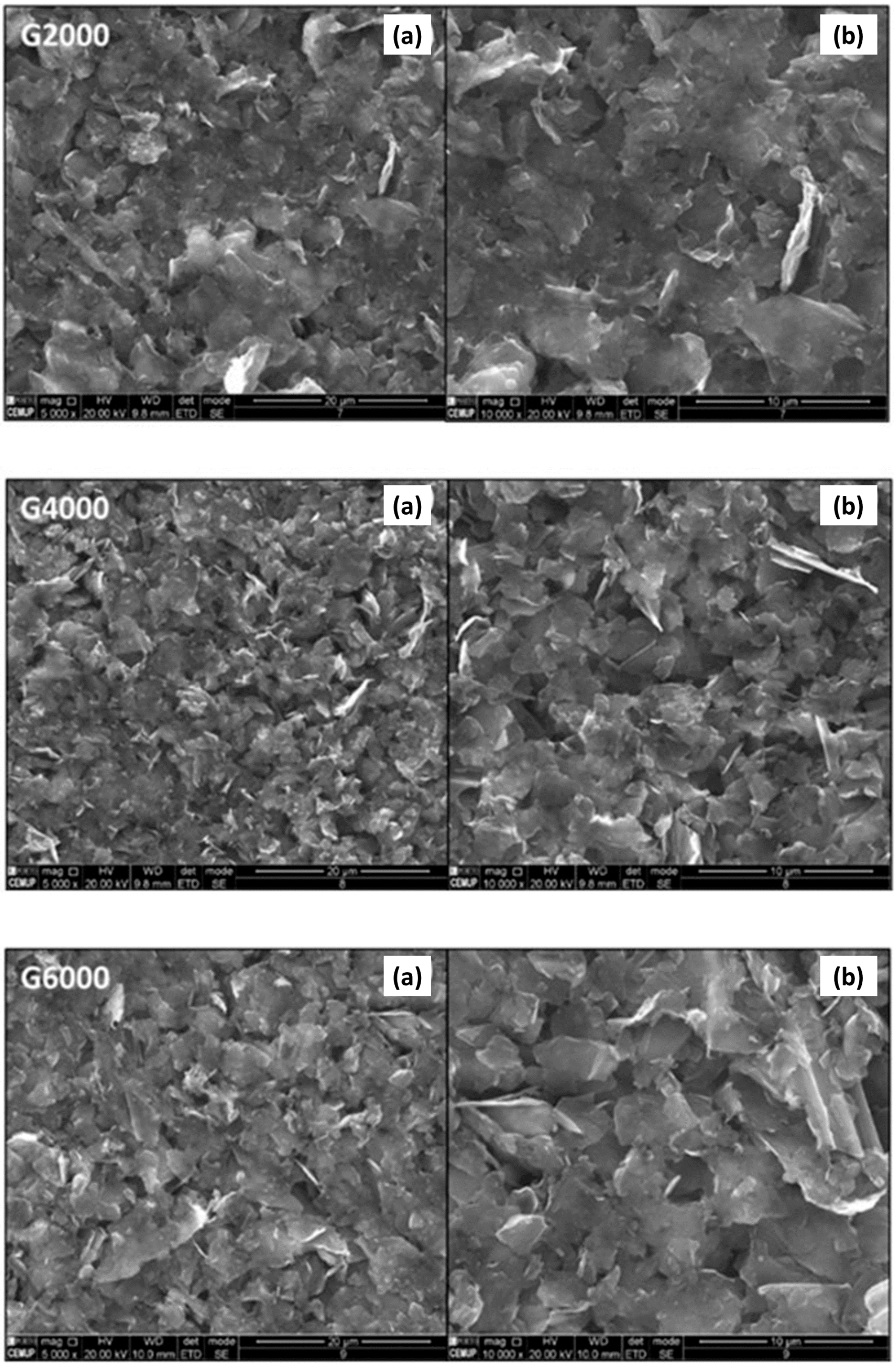


Figure S2. Electron microscopy images showing the structure of G@2000, G@4000 and G@6000 sample with 5000× (**a**), 10000× (**b**) magnification.

AFM analysis

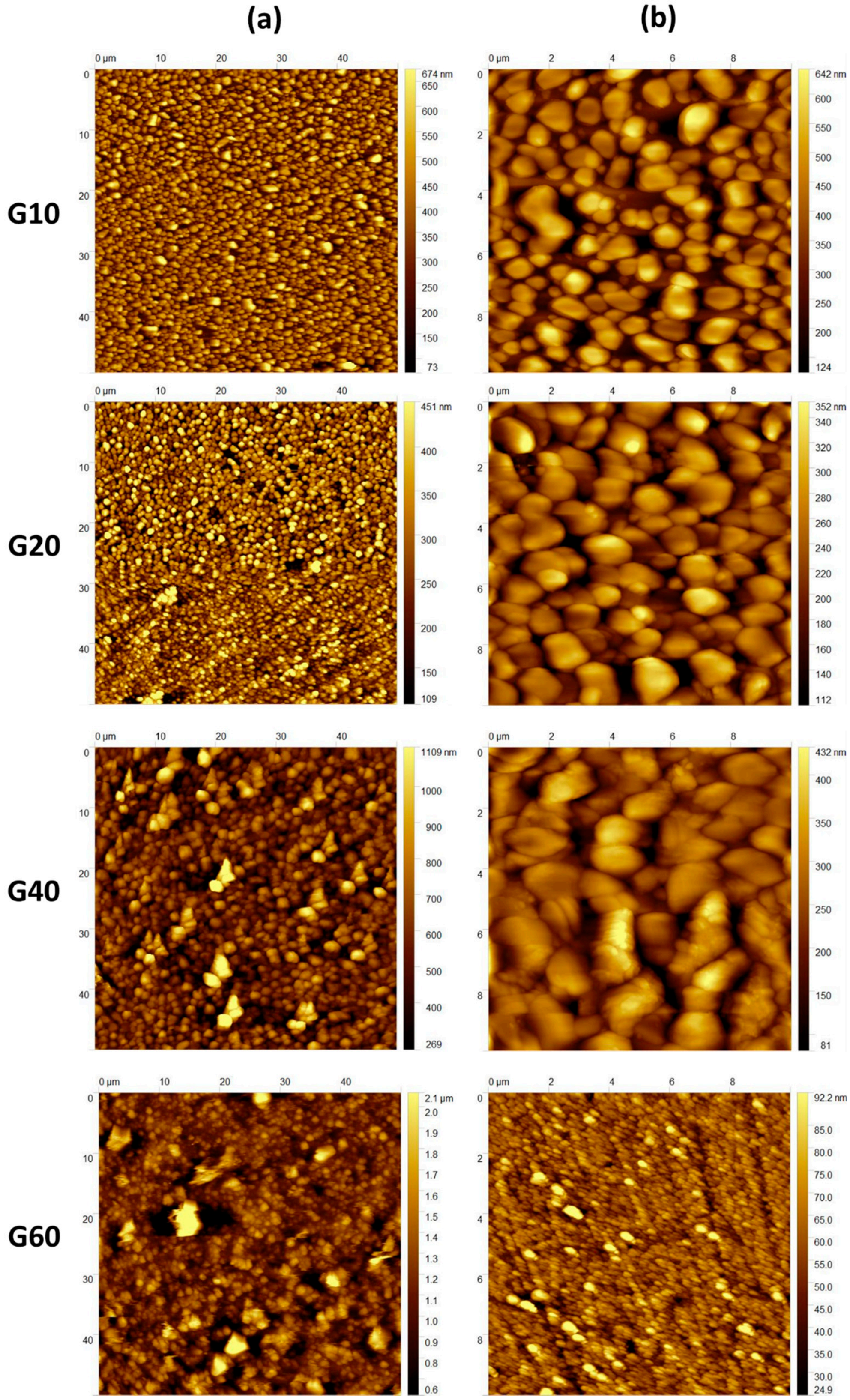


Figure S3. AFM topography images of samples G10 to G60 in GC substrate at 50 µm x 50 µm (**a**) and 10 µm × 10 µm (**b**) resolution.

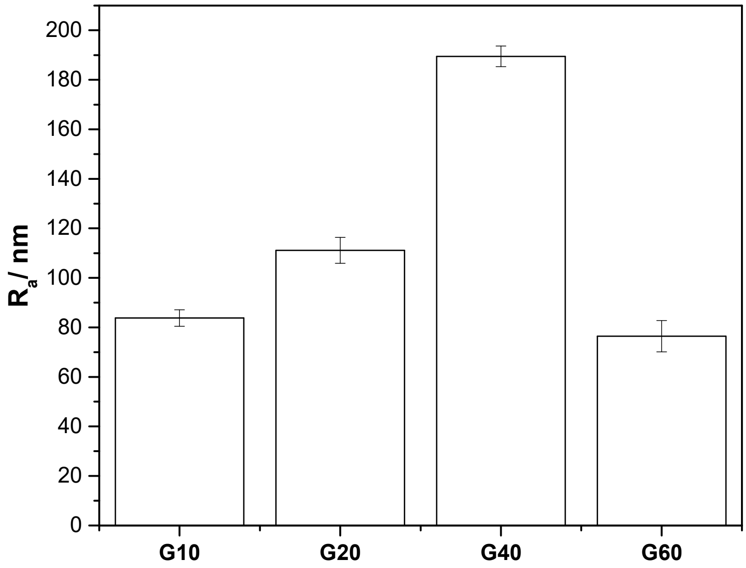
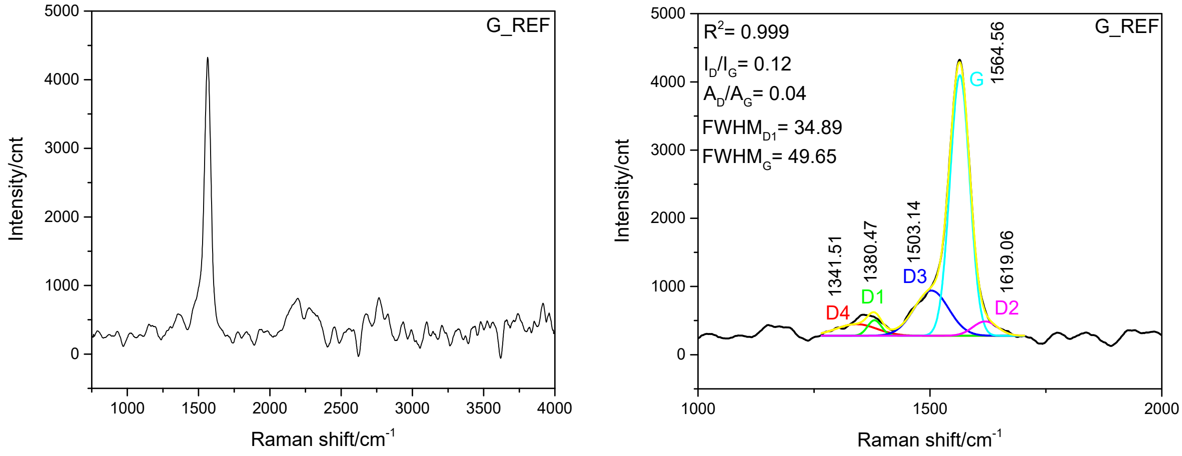


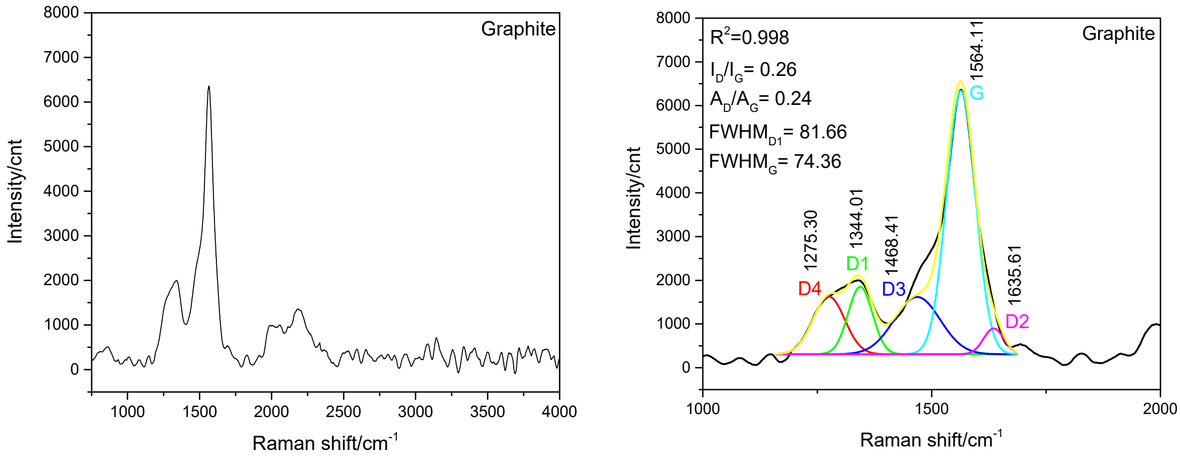
Figure S4. Surface roughness (Ra) obtained from the AFM images for Samples G10 to G60, at 50 μm × 50 μm resolution.

Raman Analysis



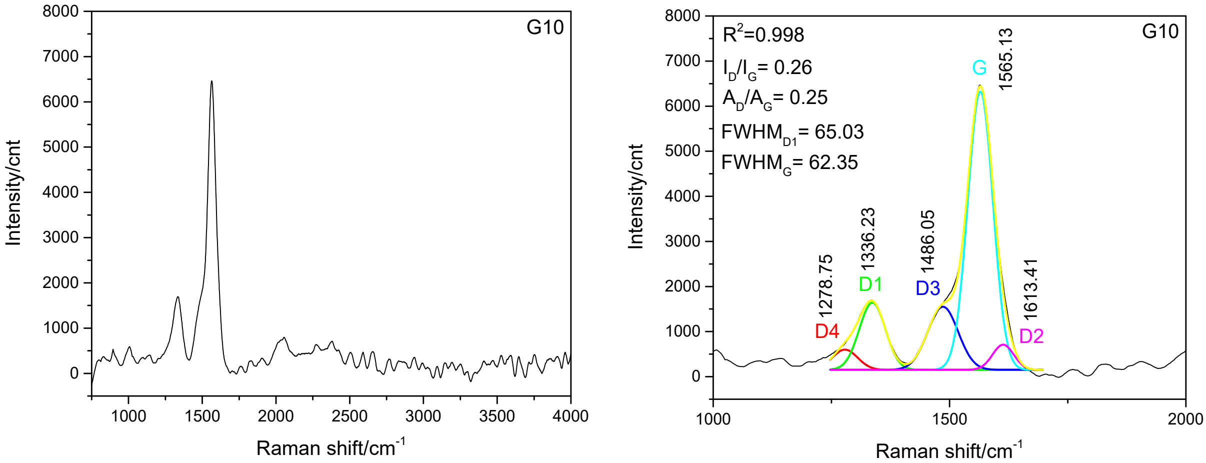
(a) (b)

Figure S5. Raman spectra of G_REF (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G_REF (**b**). The sum of the deconvolution is marked with yellow line.



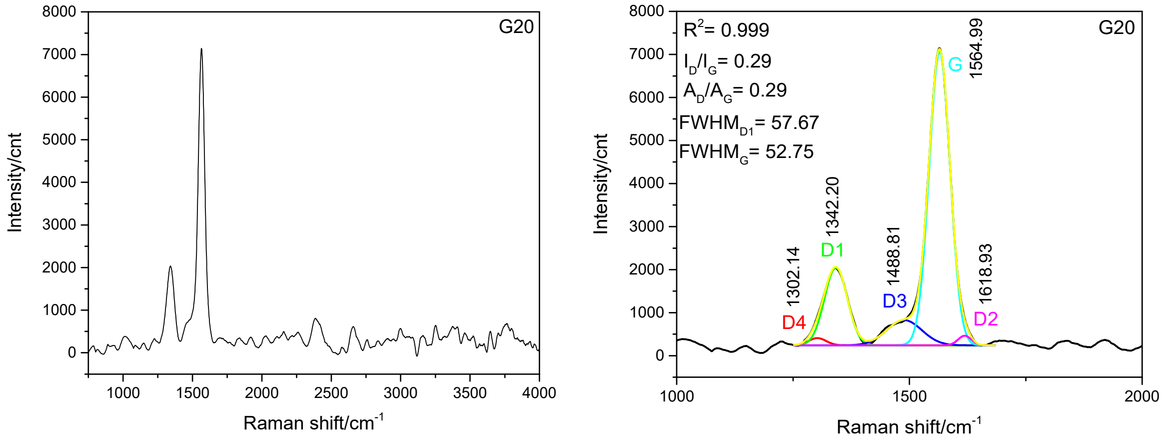
(a) (b)

Figure S6. Raman spectra of graphite (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by graphite (**b**). The sum of the deconvolution is marked with yellow line.



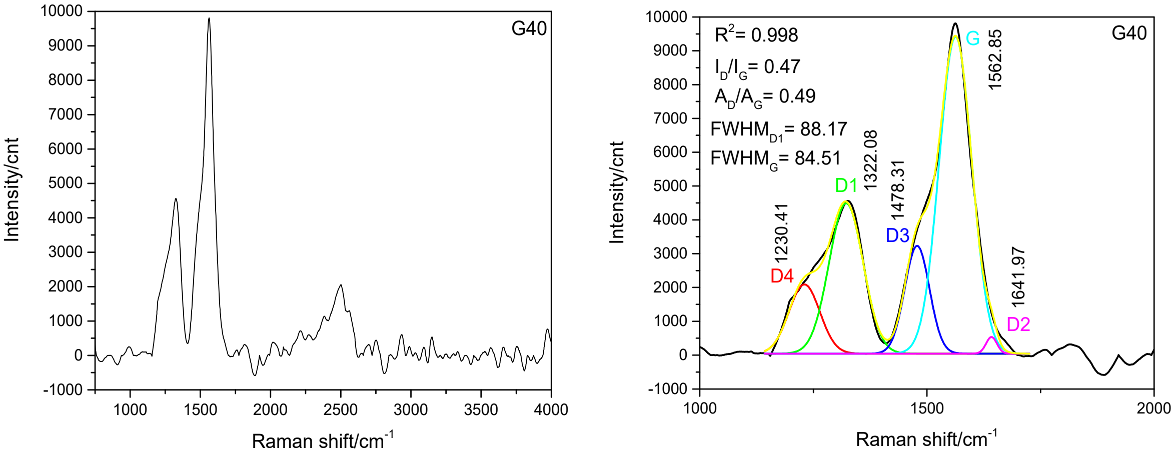
(a) (b)

Figure S7. Raman spectra of G10 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G10 sample (**b**). The sum of the deconvolution is marked with yellow line.



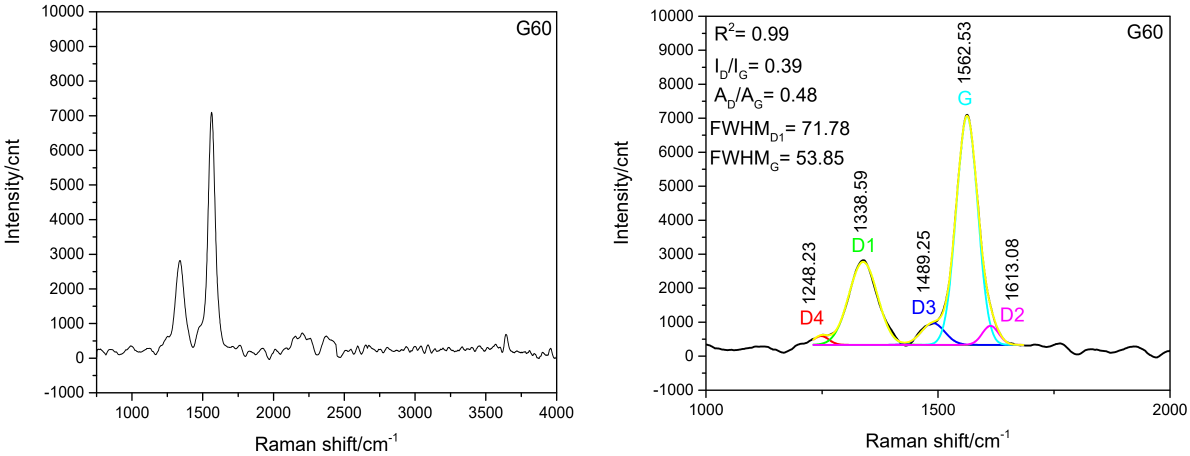
(a) (b)

Figure S8. Raman spectra of G20 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G20 sample (**b**). The sum of the deconvolution is marked with yellow line.



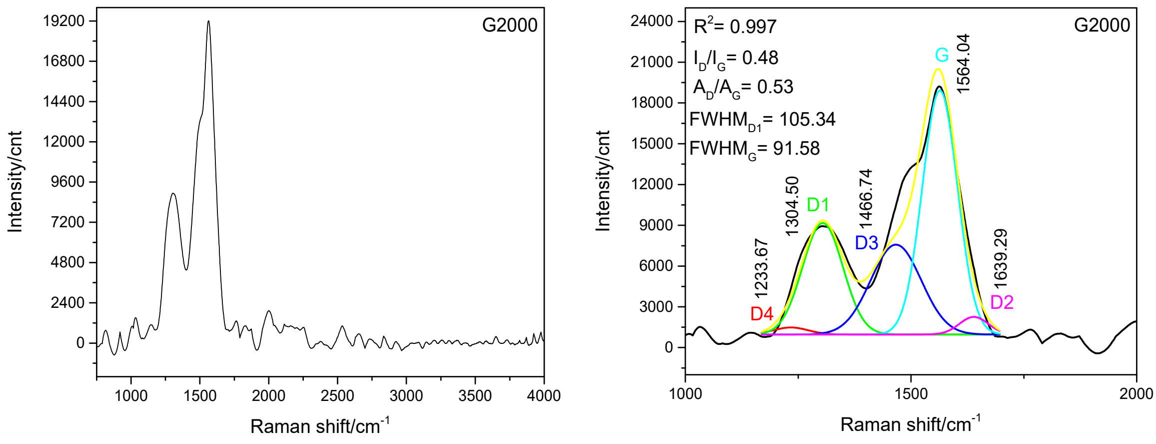
(a) (b)

Figure S9. Raman spectra of G40 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G40 sample (**b**). The sum of the deconvolution is marked with yellow line.



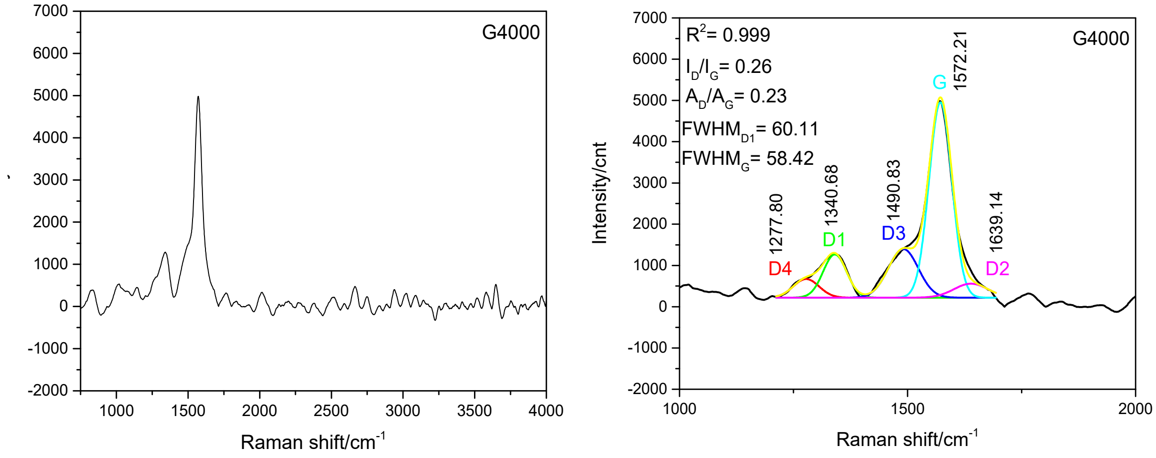
(a) (b)

Figure S10. Raman spectra of G60 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G60 sample (**b**). The sum of the deconvolution is marked with yellow line.



(a) (b)

Figure S11. Raman spectra of G@2000 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G@2000 sample (**b**). The sum of the deconvolution is marked with yellow line.



(a) (b)

Figure S12. Raman spectra of G@4000 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G@4000 sample (**b**). The sum of the deconvolution is marked with yellow line.

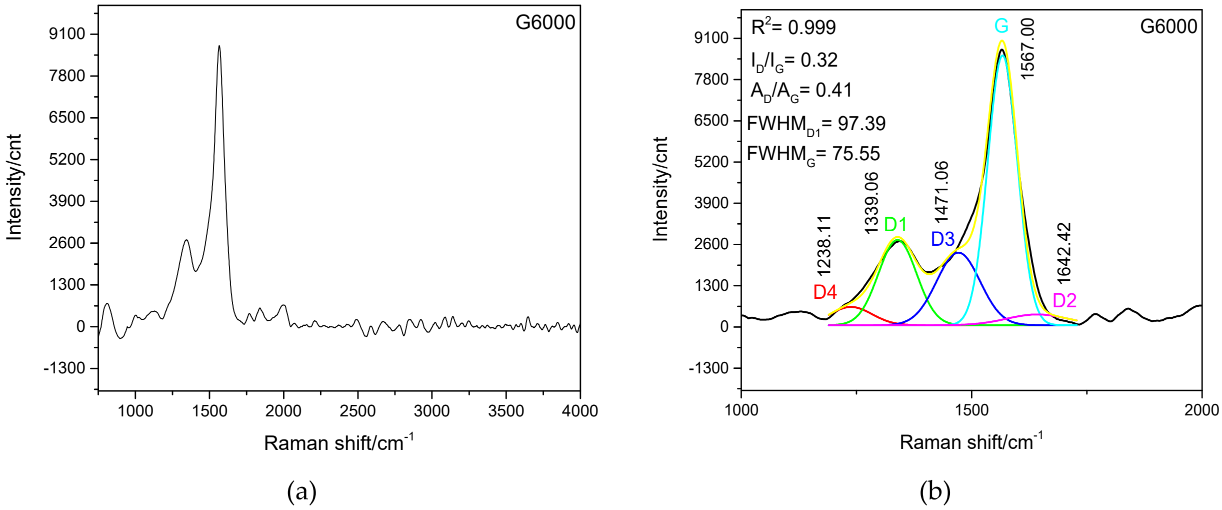


Figure S13. Raman spectra of G@6000 sample (**a**) and the deconvolution of the peaks from the 1st order Raman region of the signal emitted by G@6000 sample (**b**). The sum of the deconvolution is marked with yellow line.

Table S1. Raman data related to the G and D bands locations and ID/IG ratio for all the studied carbon materials.

	G band/ cm $^{-1}$	**D band/ cm $^{-1}$**	**I_D/ I_G**
G_REF	1564.56 ± 0.18	1380.47 ± 0.81	0.15
Graphite	1564.10 ± 0.10	1344.00 ± 3.63	0.26
G10	1565.13 ± 0.73	1336.67 ± 2.41	0.26
G20	1565.00 ± 0.06	1342.20 ± 1.13	0.29
G40	1562.85 ± 0.29	1322.08 ± 0.79	0.48
G60	1562.54 ± 0.09	1338.59 ± 0.11	0.39
G@2000	1564.06 ± 3.76	1304.50 ± 4.51	0.48
G@4000	1572.21 ± 0.42	1340.69 ± 2.17	0.26
G@6000	1567.00 ± 0.71	1339.06 ± 3.33	0.32

Electrochemical studies: IKA ULTRA-TURRAX® Tube Drive equipment

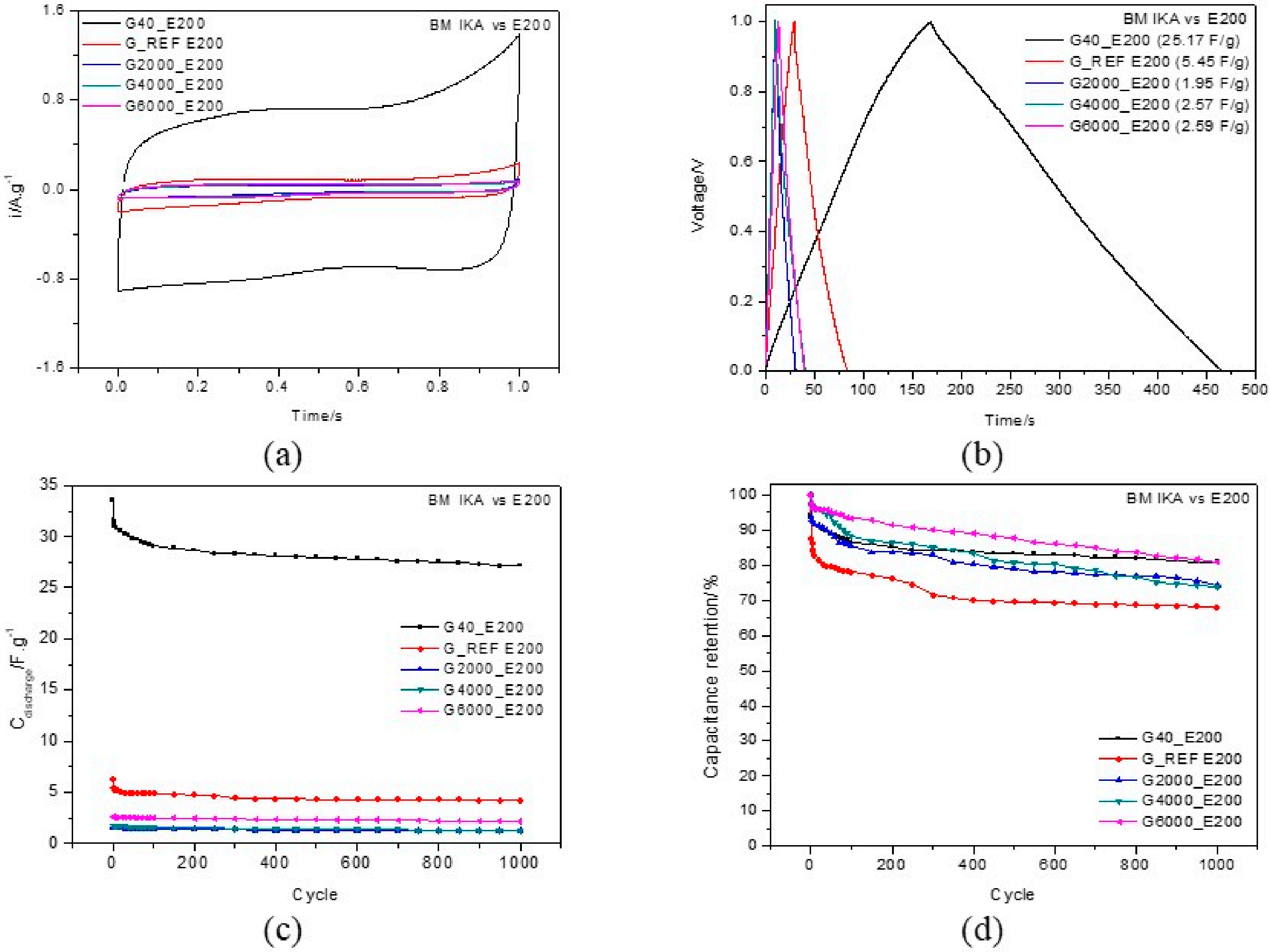


Figure S14. Ball milling effect using IKA ULTRA-TURRAX® Tube Drive for G_REF, G@2000, G@4000 and G@6000 at 30 °C, with comparison with G40 sample. (**a**) cyclic voltammetry; (**b**) galvanostatic charge-discharge curves recorded with current density 1A.g^{-1}; (**c**) discharge gravimetric capacitance for 1000 cycles; (**d**) capacitance retention.

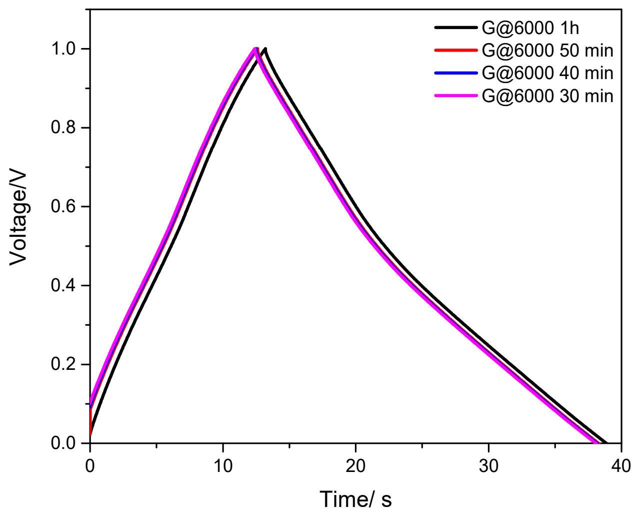
Temperature effect on capacitance

Table S2. Temperature effect on capacitance for the different ball-milled carbon materials.

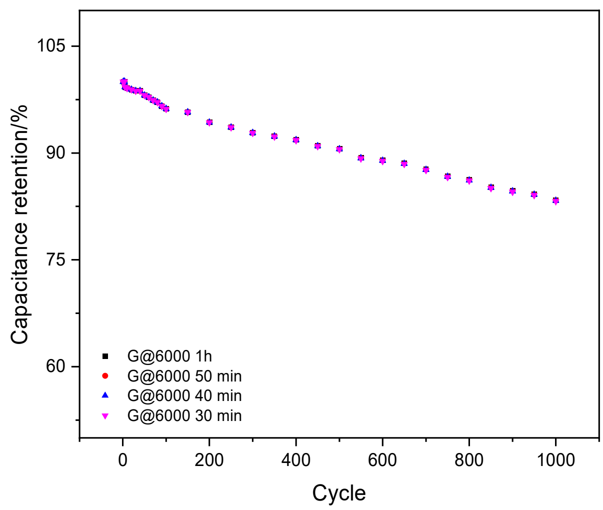
		1st Cycle				1000th Cycle			
		30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
		Capacitance (F/g)				Capacitance (F/g)			
E200	**G_REF**	**5.45**	**6.85**	**6.96**	**9.11**	**4.35**	**4.53**	5.16	5.9
	Graphite	4.27	4.33	4.51	5.09	1.71	1.82	2.03	2.27
	G10	2.36	2.88	3.43	4.09	2.11	2.61	3.1	3.8
	G20	24.83	25.33	25.98	26.74	19.8	22.31	23.58	25.01
	G40	25.1	25.89	26.47	27.88	23.1	24.87	25.41	26.09
	G60	4.19	5.01	5.54	5.96	3.99	4.31	4.92	5.33
	G@2000	1.95	2.8	3.89	5.01	1.28	2.41	3.07	4.38
	G@4000	2.57	3.77	4.61	5.33	1.39	3.09	4.03	4.87
	G@6000	2.59	3.91	4.84	5.55	2.35	3.64	4.31	4.97

Extra studies: IKA ULTRA-TURRAX® Tube Drive equipment

Several experiments were performed with the ULTRA-TURRAX, changing the time and the rotation rate as can be verified in the figure and table below. 1 h of treatment gave the better results, although only residual changes in the specific capacitance can be observed. For times longer than 1 h, ULTRA-TURRAX plastic vessels revealed signs of strong material wear and in some cases even the rupture of the vessel was observed. The capacitance retention after 1000 charge-discharge cycles is of 83.4% for all these conditions.



(a)



(b)

Figure S15. Ball milling time effect using IKA ULTRA-TURRAX® Tube Drive for G_REF G@6000 at 30 °C. (a) galvanostatic charge-discharge curves recorded with current density $1A.g^{-1}$; (b) capacitance retention for 1000 cycles.

Table S3. specific capacitance determined for IKA ULTRA-TURRAX® Tube Drive G@6000 with different milling time (30, 40, 50 and 60 minutes).

Samples	Specific Capacitance (F. g^{-1})
G@6000 _ 1h	2.59 ±0.31
G@6000 _ 50 min	2.58 ±0.28
G@6000 _ 40 min	2.58 ±0.17
G@6000 _ 30 min	2.57 ±0.33