

Supporting Information for:

Full graphitization of amorphous carbon by microwave heating

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1. Experimental

Materials

Activated carbon powders (product name: G60, KB) and Nickel (II) chloride (98%) were obtained from Sigma-Aldrich, USA. Graphite powder was obtained from Samchun Chemical, Korea.

The characteristics of activated carbons used in this work are listed in Table S1. Elemental analysis was performed using varioMICRO CHNS, and other characteristics were obtained from the technical information supplied by Sigma-Aldrich.

Table S1. Characteristics of activated carbon powders obtained from Sigma-Aldrich.

Sample name	G60	KB
Particle size (mesh)	100–325	100–325
Surface area (m²/g)	600	1500
Pore volume (ml/g)	0.95	2
Moisture (% , max)	12	33
Ash (%)	3.5	3
Water solubles (% , max)	0.5	1.5
Tamped bulk density (lb/ft²)	25	28
Carbon contents (wt.%)	83.25	63.50
Hydrogen contents (wt.%)	1.31	3.29
Nitrogen contents (wt.%)	0.44	0.16
Sulfur contents (wt.%)	0.17	0.04

Experimental apparatus

Microwave graphitization was achieved using the experimental system described in

our previous works.¹ The system consisted of a magnetron, an isolator, a directional coupler, an auto tuner, a quartz reactor, and gas feeders. Impregnated carbon powders were loaded onto the quartz boat, then placed in the quartz reactor. The temperature was measured using an infrared (IR) thermometer, MR1SC, manufactured by Raytek.

Sample preparation

Nickel chloride (NiCl_2) was impregnated with G60 and KB in ethanol. During the impregnation step, 6 mmol NiCl_2 (/g carbon powder) were stirred for 5 or more hours at room temperature until all solvents were evaporated. The sample was subsequently dried at 75°C for 24 hours.

Next, 1000 W and 1400 W microwave radiation was directed onto the G60 and KB samples, respectively. The reactor was filled with argon gas under normal pressure prior to turning on the microwave generator. The flow rate of the argon gas during microwave irradiation was 100 sccm.

Characterization

The carbon powder underwent structural changes before and after microwave irradiation, as observed using X-ray diffraction (XRD) methods with a CuK_α radiation source, Raman spectroscopy (Horiba Jobin Yvon, LabRam HR) using the 514.5 nm line of an argon ion laser, and by transmission electron microscopy (HR-TEM, JEOL JEM-2200FS with image Cs-corrector).

2. Temperature profile

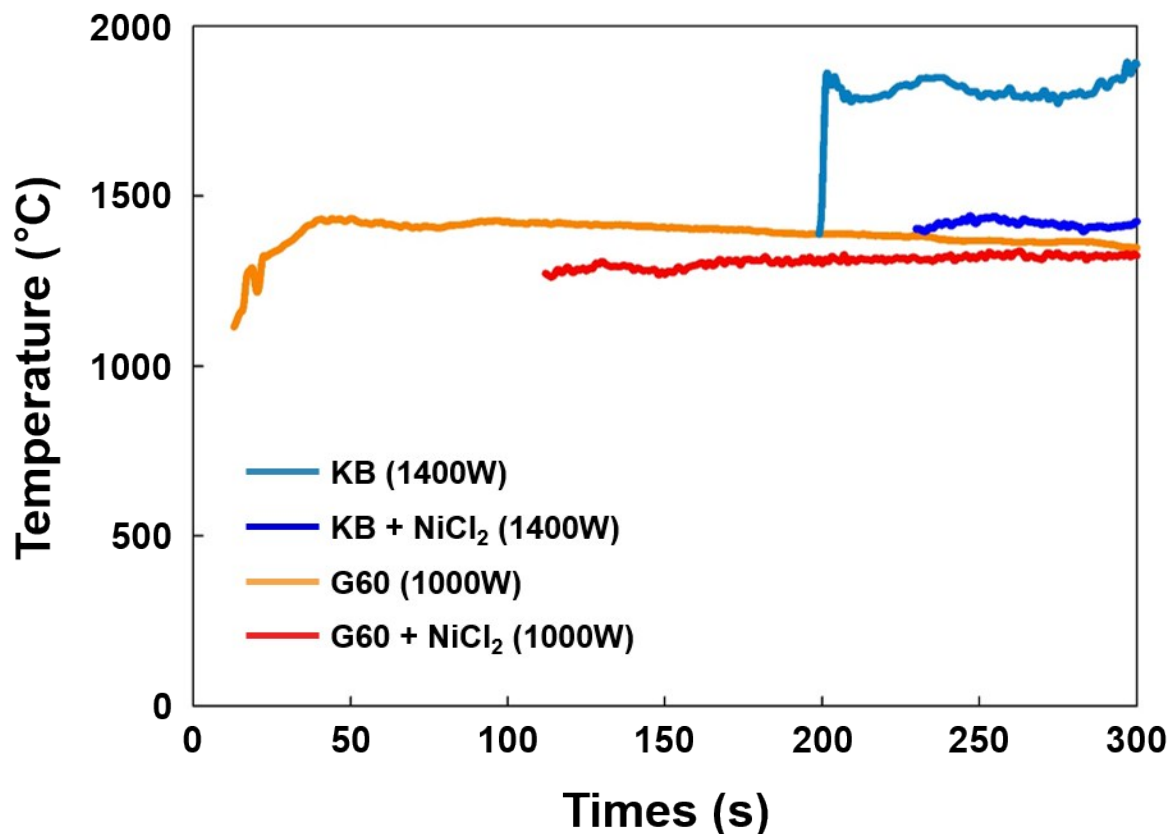


Figure S1. Temperature profiles of the carbon powders under microwave irradiation.

Figure S1 presents the temperature profiles of the activated carbon powders under microwave irradiation. Because the measurable range of the IR thermometer (MR1SC, Raytek) extended from 1000 to 3000°C, some regions of the curves at the start of irradiation were not recorded. The time required to reach beyond one thousand degrees Celsius was 13 s for pristine G60, 112 s for NiCl₂-impregnated G60, 199 s for pristine KB, and 230 s for NiCl₂-impregnated KB. The fraction of the carbon (microwave-absorbing part of the sample) was assumed to be related to the time. Among the pristine activated carbon powders, G60, which had a higher carbon content (See Table S1) required shorter times than did KB to reach a temperature

exceeding one thousand degrees Celsius. As the fraction of carbon decreased upon impregnation with NiCl₂, the time required to reach a temperature exceeding one thousand degrees Celsius became longer within the same activated carbon powder.

The maximum temperature and the average temperature (with the exception of the unrecorded region) are listed in Table S2.

Table S2. Maximum temperature (T_{\max}) and average temperature (T_{avg}) of the activated carbon powders under microwave irradiation.

Sample	KB	KB+NiCl₂	G60	G60+NiCl₂
Microwave condition	1400 W 5 min	1400 W 5 min	1000 W 5 min	1000 W 5 min
T_{\max} (°C)	1893	1441	1433	1338
T_{avg} (°C)	1806	1418	1388	1308

3. The state of NiCl₂ after impregnation and drying.

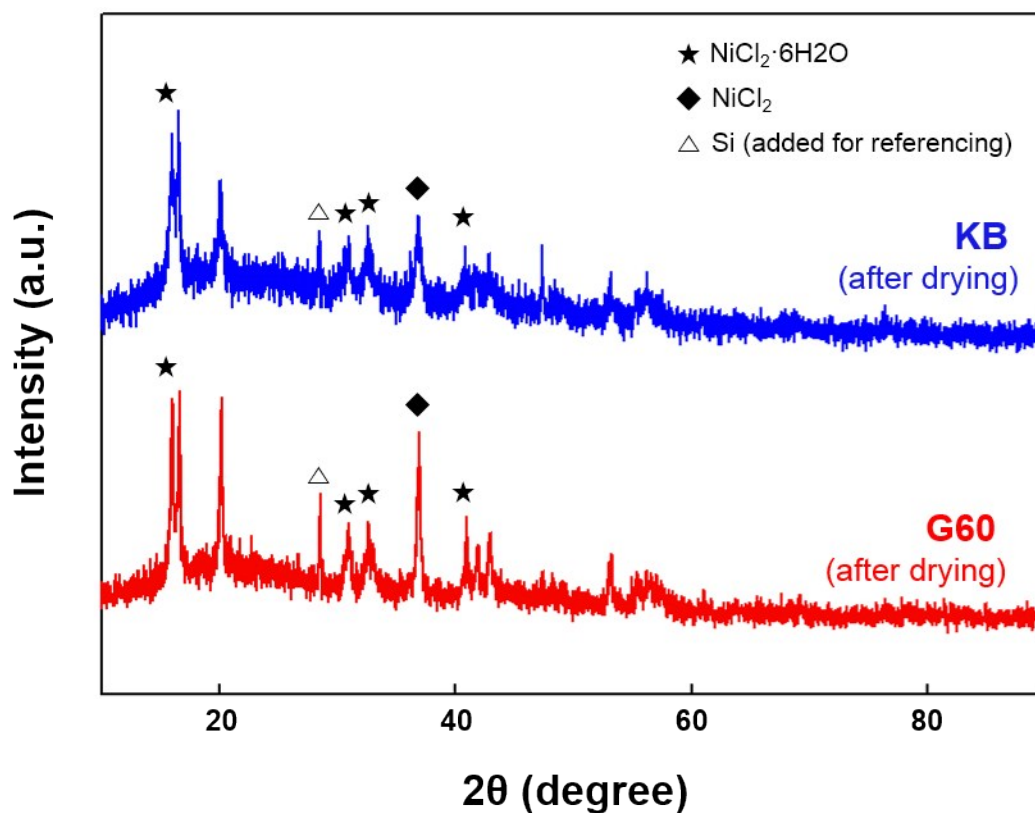


Figure S2. XRD patterns of the activated carbons after NiCl₂ impregnation and drying. Nickel (II) chloride (NiCl₂), nickel chloride hexahydrate (NiCl₂·6H₂O) peaks and no nickel peaks (44.60°, 51.91°, 76.81°) were observed (Si was added to adjust the position.).

The full XRD patterns of the activated carbon powders after NiCl₂ impregnation and drying are shown in Figure S2. With the exception of silicon, which was added as a reference material, nickel (II) chloride (NiCl₂), nickel chloride hexahydrate (NiCl₂·6H₂O) peaks were mainly observed. Because there was no Ni peaks, nickel particles were not formed before microwave irradiation.

4. Full XRD patterns of the activated carbon powders, as measured after microwave graphitization

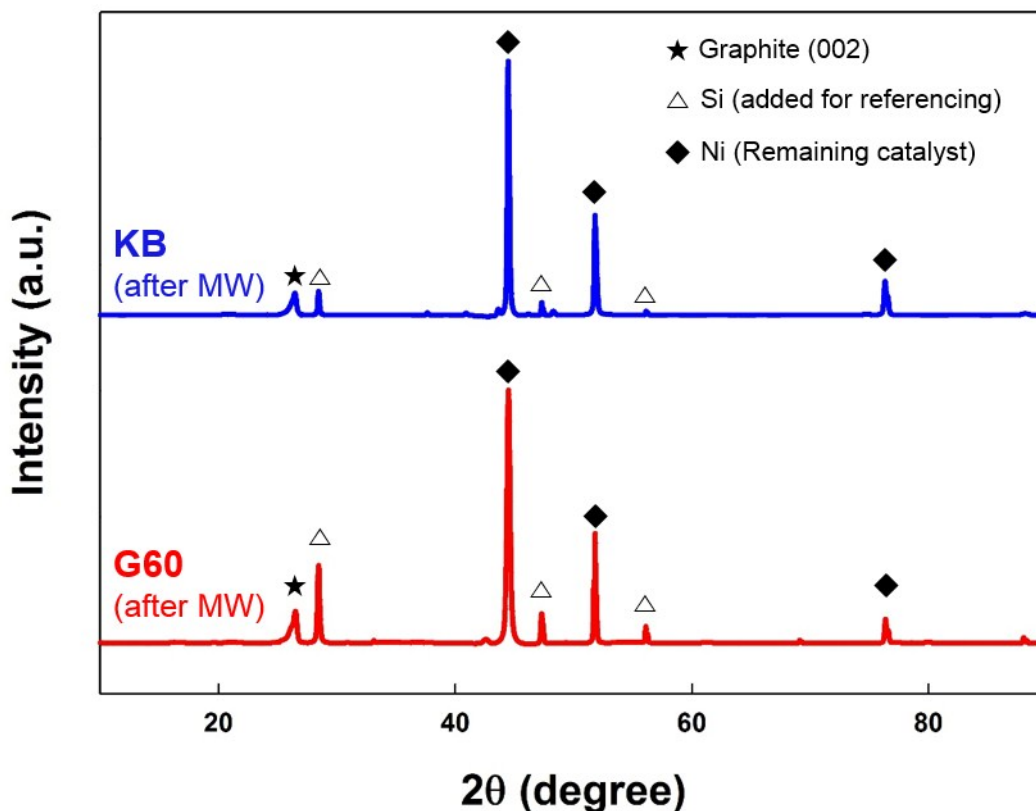


Figure S3. XRD patterns of the activated carbons after microwave graphitization with NiCl_2 . Only graphite and the Ni peaks were observed. (Si was added to adjust the position.)

The full XRD patterns of the activated carbon powders after microwave graphitization in the presence of NiCl_2 impregnation are shown in Figure S3. With the exception of silicon, which was added as a reference material, only graphite and nickel peaks were observed.

5. TGA and the remaining nickel content in the activated carbon powders

The contents of the nickel remaining after microwave graphitization were analyzed by thermogravimetric analysis (TGA). The TGA measurements were conducted in air with a heating rate of 10°C/min.

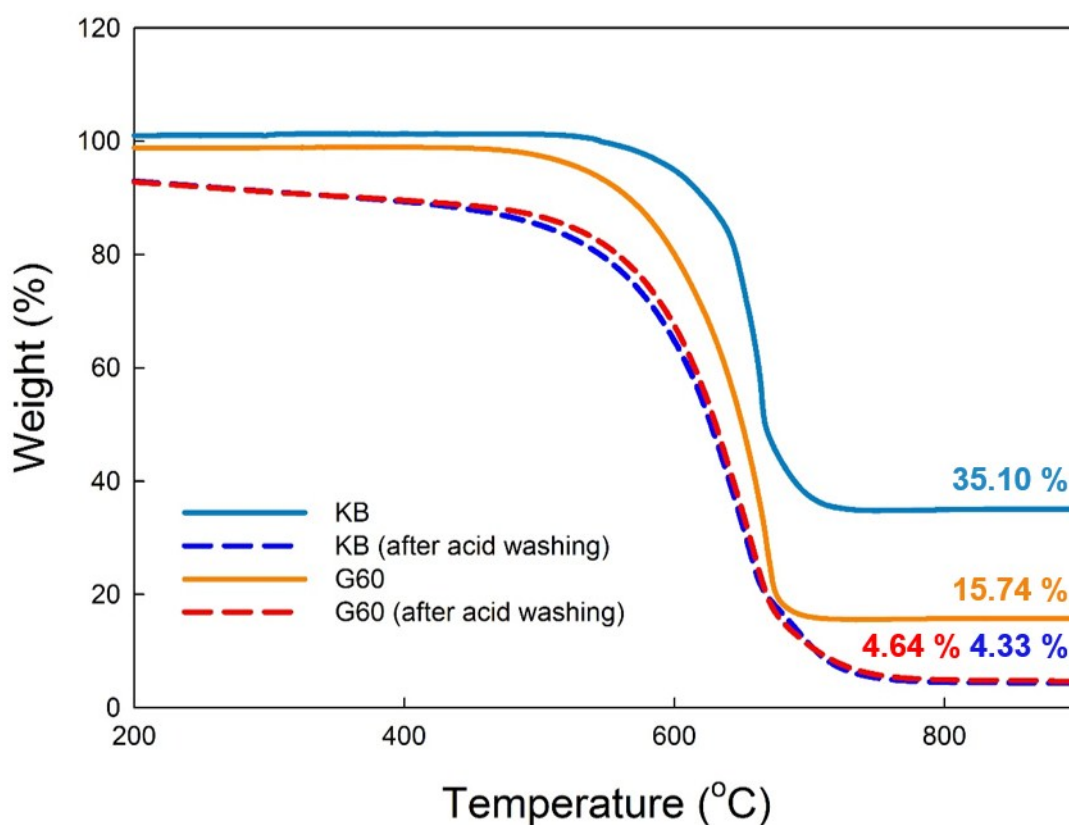


Figure S4. TGA results obtained from the microwave-graphitized activated carbon samples before and after acid washing. After acid washing (red and blue lines), the weight percent of the remaining metal was less than 5%.

Because only graphite and nickel were present after graphitization, according to the XRD studies (Figure S3), the entire sample remaining at 900°C was assumed to be nickel. After microwave graphitization of the NiCl₂-impregnated sample, the weight percent of nickel was

15.74% in G60 and 35.10% in KB. Most of the nickel was removed using a simple acid washing step (1 M HNO₃).

6. Interlayer spacing calculations

The interlayer spacings (d) of each sample were calculated using Bragg's law ($2d\sin\theta = n\lambda$).

The position of the peak corresponding to the graphite (002) peak was substituted for θ , and the wavelength of Cu K α 1 (1.540598 Å) was substituted for λ . The graphite (002) peak position and the calculated interlayer spacing of each sample are shown in Table S3.

Table S3. Graphite (002) peak position (2θ) and the interlayer spacings (d_{002}) of the carbon powders.

the Sample	Impregnation	Microwave	2θ	d_{002} (Å)
G60	No	No	23.45°	3.7901
	No	1000 W, 5 min	25.55°	3.4833
	NiCl ₂ 6 mmol	1000 W, 5 min	26.50°	3.3610
KB	No	No	24.57°	3.6200
	No	1400 W, 5 min	25.43°	3.4993
	NiCl ₂ 6 mmol	1400 W, 5 min	26.46°	3.3662
Graphite	No	No	26.50°	3.3612

7. Microwave heating in the absence of the catalysts

The activated carbon powders were subjected to microwave heating without a catalyst, for comparison purposes. The XRD patterns near the graphite (002) peak of G60 and KB after microwave irradiation without NiCl_2 are shown in Figure S6 (orange dash line). The microwave irradiation conditions for the NiCl_2 -unimpregnated G60 and KB samples were exactly the same as those applied to the NiCl_2 -impregnated G60 and KB samples (G60: 1000 W for 5 min under an argon atmosphere, KB: 1400 W for 5 min under an argon atmosphere).

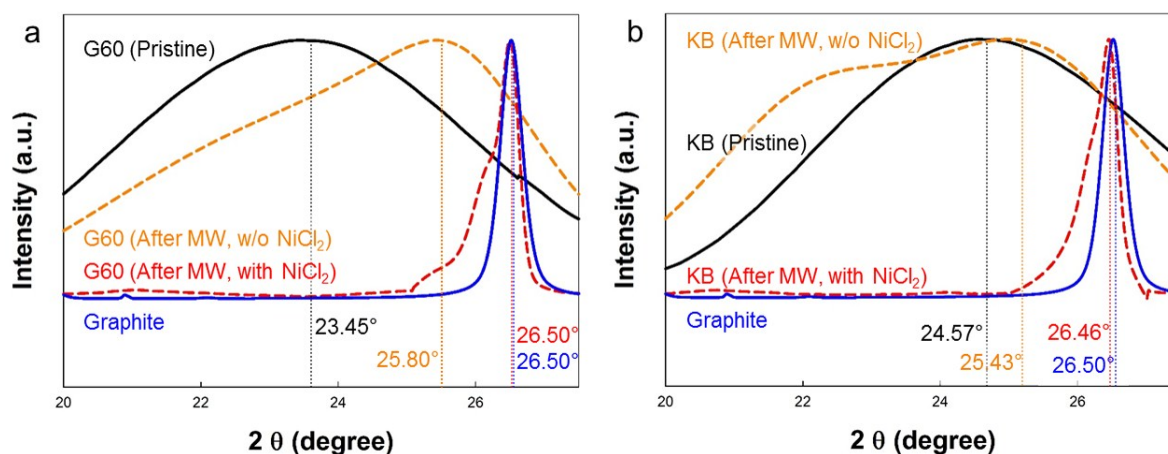


Figure S5. XRD patterns near the graphite (002) peak of G60 (a) and KB (b) before and after microwave irradiation.

Without the metal catalyst, the activated carbon powders only showed slight changes in their crystalline structures, as observed using XRD methods. The position of the (002) peak of G60 moved toward higher angles after microwave irradiation in the absence of NiCl_2 (25.80°), but the position was much lower than the position of graphite (26.50°) or of microwave-graphitized G60 in the presence of NiCl_2 (26.50°). Also, the breadth of the (002) peak

remained similar to that of pristine G60. The KB appeared to undergo a partial transformation. Noticeable peak separation was observed, and the relative intensity at lower angles (around 22°) increased after normalization by the maximum intensity.

8. Heating method, temperature, and d-spacing of the various carbon samples presented in Figure 3a.

Table S4. d-spacing of the carbon samples after heat treatment. (PFO: Pyrolysis fuel oil-derived isotropic pitch ⁴, NMP: Naphthalene-derived mesophase pitch ⁴. Pitch coke I: carbonized coal-tar pitch ⁵, OIL: Cyclohexane soluble fraction after distillation of solvent, consists of oils ⁶, PREAS: Vacuum-dried preasphaltenes of the benzene-insoluble portion of pitch ⁶, PVC: Polyvinyl chloride ⁷, Pitch coke II: carbonized pitch ⁷.)

Sample name	Heating method	Temperature (°C)	Time	d-spacing (Å)
G60 (+NiCl ₂)	Pristine			3.7901
	Microwave	1308	5 min	3.3610
KB (+NiCl ₂)	Pristine			3.6200
	Microwave	1418	5 min	3.3612
PFO	Pristine			3.50
	Microwave	1170	30 min	3.43
NMP	Pristine			3.53
	Microwave	1170	30 min	3.42
Pitch coke	Thermal	1250	25 h	3.43
		2200	25 h	3.39
		2300	25 h	3.38
OIL	Thermal	1000	1 h	3.4660
		2000	1 h	3.4170
		3000	1 h	3.3610
PREAS	Thermal	1000	1 h	3.4930
		2000	1 h	3.4240
		3000	1 h	3.3710
PVC	Thermal	2140	2 h	3.3870
Pitch coke II	Thermal	2140	2 h	3.3950

The heating method, heating temperature, heating time, and d-spacing of each point are listed in Table S4.

In general, the d-spacing decreased as the heat treatment temperature increased. Thermal graphitization without a catalyst achieved full graphitization around 3000°C.⁸ The d-spacings of the OIL and PREAS samples after thermal graphitization at 3000°C for 1 h were 3.3610 Å and 3.3710 Å. Microwave heating changed the crystallinity of the PFO and NMP at lower temperatures and over shorter periods of time (the d-spacing of PFO was 3.43 Å and that of NMP was 3.43 Å after 30 min of microwave heating at about 1170°C) compared to the thermal heating (the d-spacings of the OIL and PREAS samples were 3.4170 Å and 3.4240 Å after thermal heating at 2000°C for 1 h); however, the d-spacings were still too large to claim full graphitization.

9. Comparison between the microwave graphitization and thermal graphitization processes in terms of processing time

The merits of the microwave graphitization in terms of time required to reach completion were examined by comparing the microwave process conditions to the thermal heating conditions, applied to a NiCl₂-impregnated KB sample for different heat treatment times. The experimental conditions applied to achieve microwave heating and thermal heating are shown in Table S5.

Table S5. Experimental conditions for microwave and thermal heating.

Sample number	1	2	3	4
Heating method	Microwave	Thermal (Lindberg blue M)		
Power	1400 W	8000 W		
T _{max} ^a	1441°C	1000°C		
t _m ^b	70 s	5 min	30 min	60 min
t _h ^c	230 s	30 min	30 min	30 min
t _t ^d	5 min	35 min	60 min	90 min

^a Maximum temperature

^b Time maintained at or over 1000°C

^c Time required to heat up to 1000°C

^d Total processing time (t_m+t_h)

The maximum temperatures reached during microwave heating or thermal heating differed for two reasons: 1. 1400 W was the minimum power needed to exceed one thousand degrees Celsius in the NiCl₂-impregnated KB sample within 5 min. 2. The maximum operation temperature of the furnace was 1100°C.

These experiments compared the new method (catalytic graphitization using microwave

heating) to the conventional method (catalytic graphitization using thermal heating) used for graphitization. We also compared the new method with more general thermal graphitization conditions (1000°C or less).

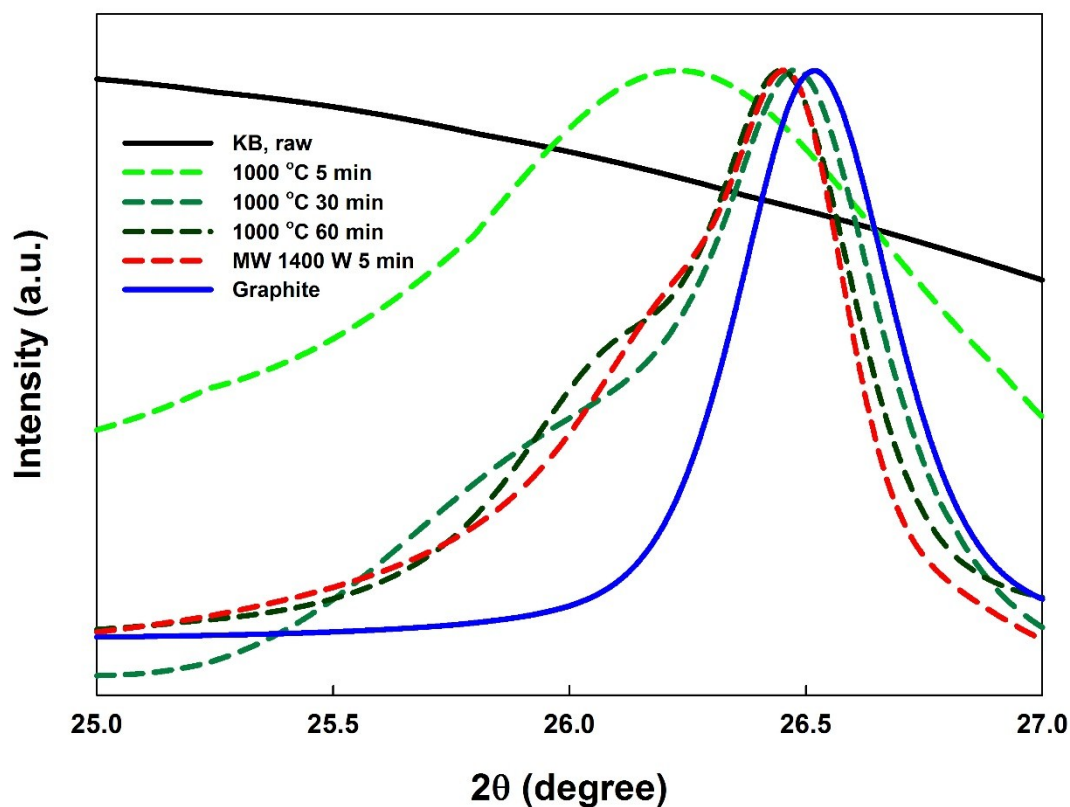


Figure S6. (002) peak obtained from the KB sample after thermal and microwave graphitization. Thermal graphitization proceeded for 5, 30, and 60 min at 1000°C, and microwave graphitization proceeded for 5 min at a 1400 W microwave power. The (002) peak of the raw material (KB) and graphite are presented for reference purposes.

As shown in Figure S7, microwave graphitization displayed tremendous advantages in terms of the time required to complete the process. Only 5 min of microwave irradiation provided similar structural changes as 30 min of the conventional process (thermal graphitization). In Figure S7, the heating-up time required for the thermal heating process was excluded. If we

consider this additional time and compare the total processing time (t_i), the gap between the time required for the microwave graphitization and thermal graphitization is much larger.

10. Commercially available plate-type flow reactor.

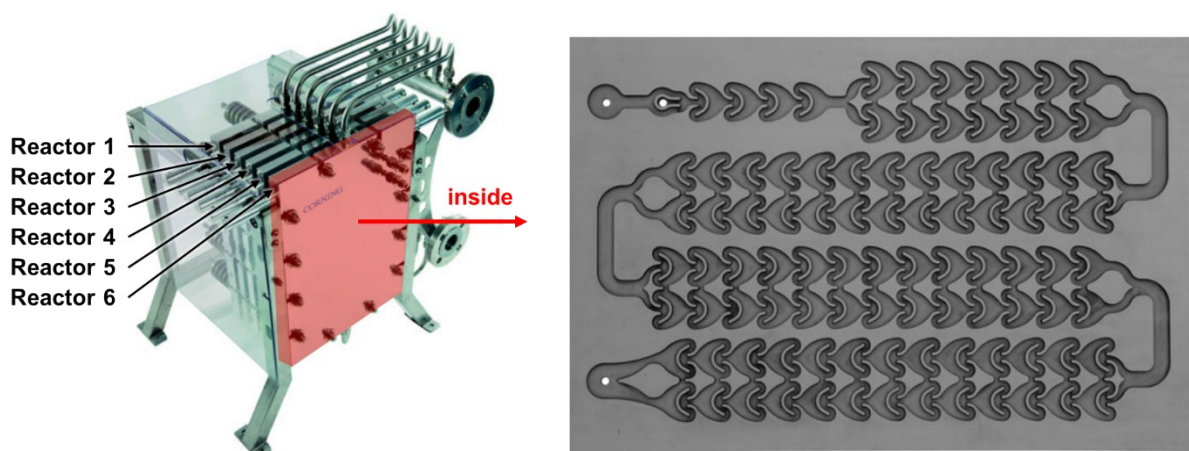


Figure S7. Advanced-flow ceramic reactor of Corning.⁹

A hint for the scale-up of microwave reactor can be obtained from the plate-type flow reactor which is commercially available (Fig. S8). This reactor was introduced to maximize the heat delivery from the heating fluid to the reactants. A similar approach can be applied to the scale-up of a microwave reactor.

11. The effect of q on the calculated dielectric loss factor.

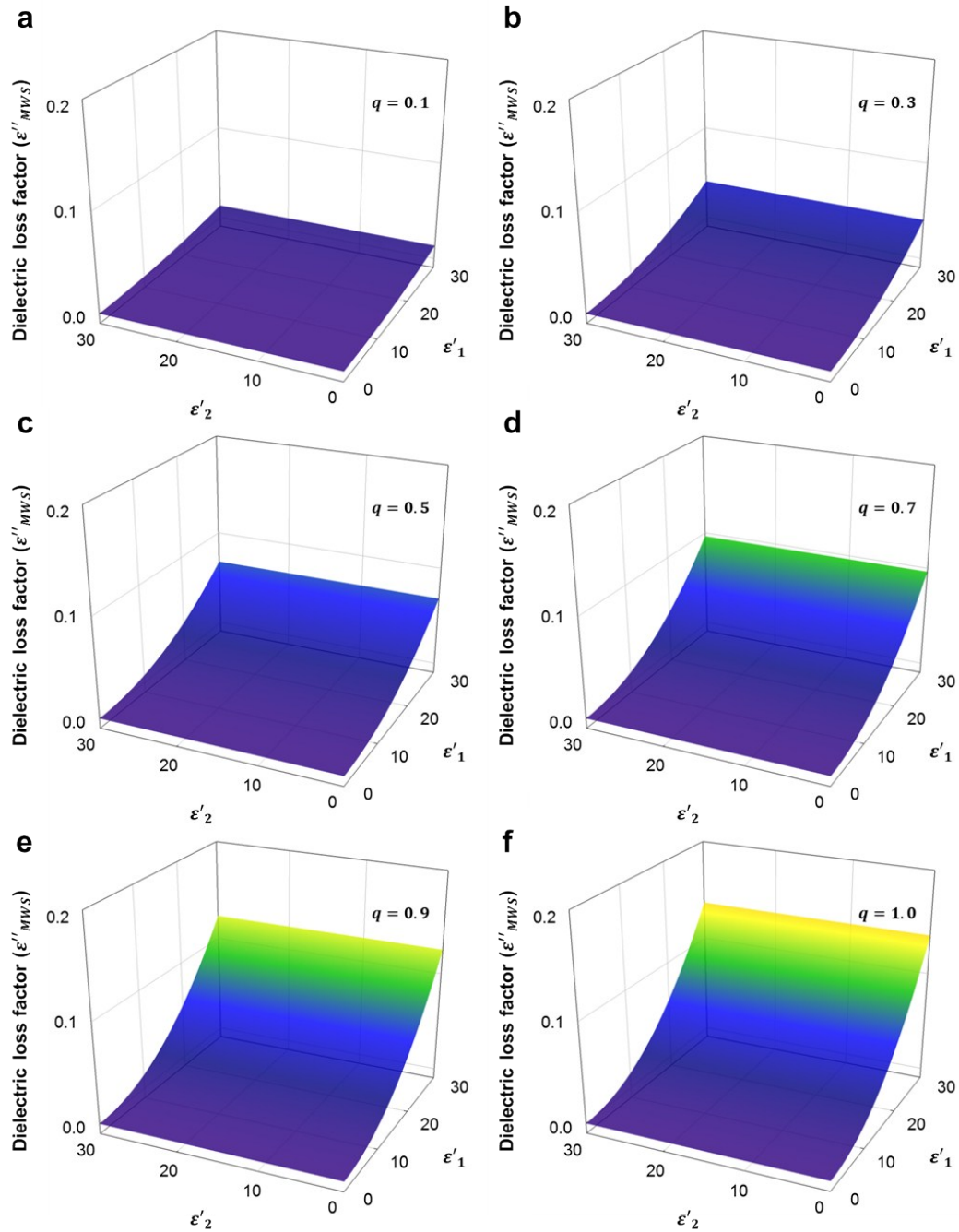


Figure S8. Calculated dielectric loss factor with various dielectric constants when (a) $q=0.1$, (b) $q=0.3$, (c) $q=0.5$, (d) $q=0.7$, (e) $q=0.9$ and (f) $q=1.0$. ($\sigma_2 = 2000 S/cm$, $n = 15$, and $f = 2.45 GHz$)

12. The effect of n on the calculated dielectric loss factor.

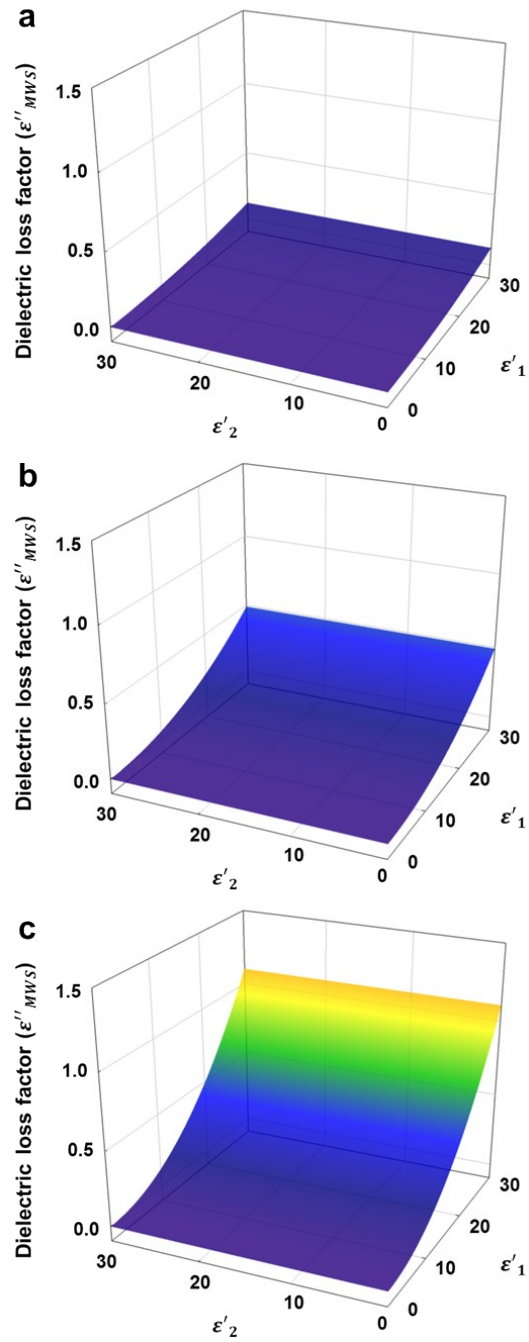


Figure S9. Calculated dielectric loss factor with various dielectric constants when (a) $n=10$, (b) $n=20$ and (c) $n=30$. ($\sigma_2 = 1000 \text{ S/cm}$, $q = 1$, and $f = 2.45 \text{ GHz}$)

13. The effect of n on the calculated dielectric loss factor.

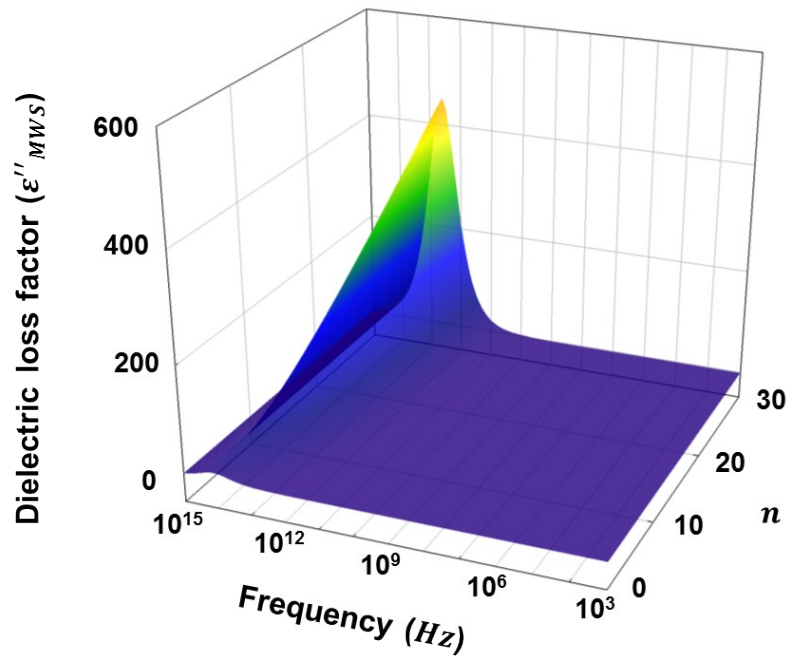


Figure S10. Calculated dielectric loss factor with varying frequency (f) and eccentricity (n). ($\epsilon'_1 = \epsilon'_2 = 30$, $\sigma_2 = 2000 S/cm$, and $q = 1$)

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