Electronic Supplementary Information for

Surface Defect Healing in Annealing from Nanoporous Carbons to Nanoporous Graphenes

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Nitrogen Physisorption

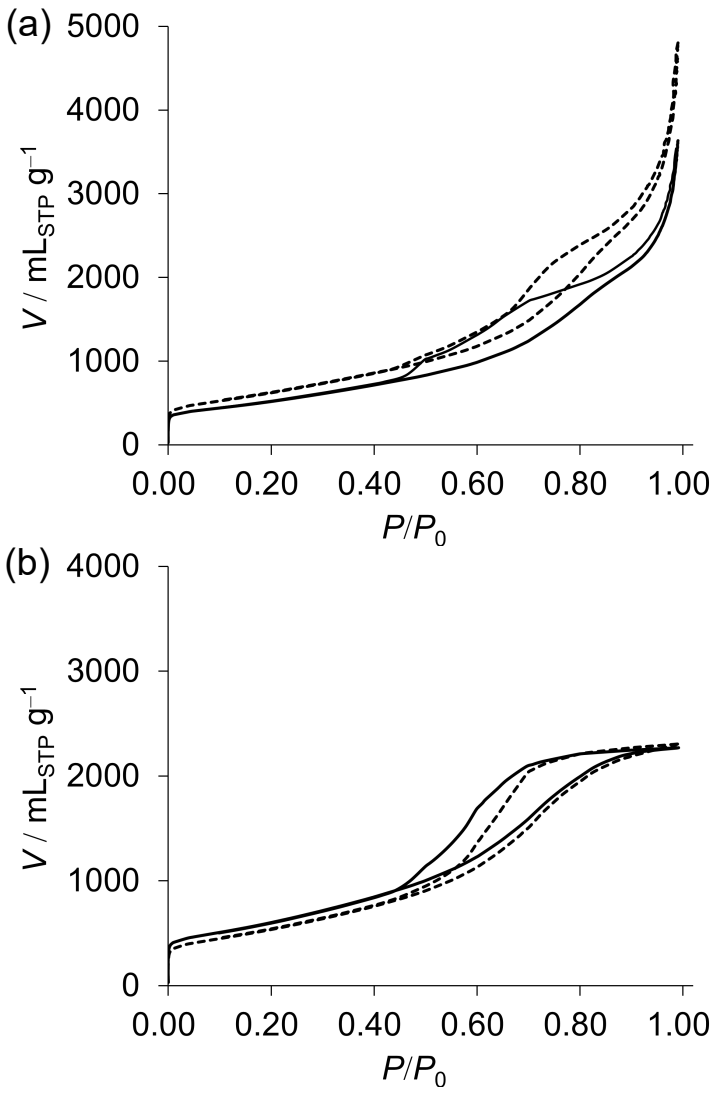

Figure S1. N_2 physisorption at 77 K of **NPC**s (dashed line) and **NPG**s (solid line) obtained from (a) θ-Al_2O_3 and (b) γ-Al_2O_3 as the templates.

Temperature-Programmed Desorption

The amounts of H_2, H_2O, CO, and CO_2 evolved during the pyrolysis were quantified by TPD methods as previously reported.[S2]

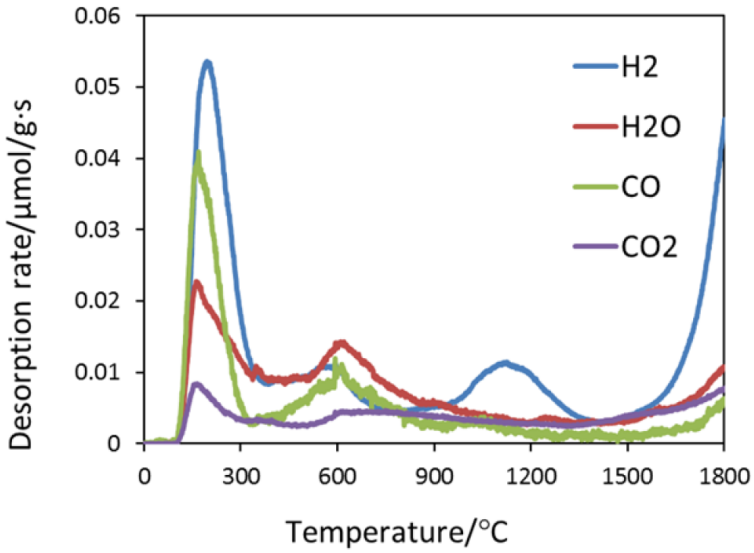

Figure S2. The representative TPD profile of **NPG** synthesized using γ-Al_2O_3 as the template.

The defect density *per* hexagon based on the TPD λ_{TPD} in the SI unit was calculated with the total amount of evolved gases N_{total} in mol g^{-1} including H_2, CO, and CO_2, and gravimetric surface area S_{BET} in m^2 g^{-1} as,

$$\lambda_{TPD} = N_{total} / S_{BET} \text{ [mol m}^{-2}\text{]} \quad \text{(S1)}$$

We can convert the SI unit-based λ_{TPD} to molecule-based λ_{TPD} by multiplying the specific area of a graphene hexagon S_h and Avogadro constant N_A (6.022×10^{23} mol^{-1}) as,

$$\lambda_{TPD} = N_{total} N_A S_h / S_{BET} \text{ [per hexagon]} \quad \text{(S2)}$$

where $S_h = 0.0523 \times 10^{-18}$ m^2 is calculated using the C=C bond length (0.142 nm) in the hexagons. The obtained λ_{TPD} values based on Eq. S2 are listed in Table 1 of the manuscript.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of the carbon/alumina composites was conducted using a thermogravimeter (Shimadzu, DTG-60H) operating from 300 to 1173 K at a rate of 10 K min^{-1} under a steady flow of air (50 mL min^{-1}).

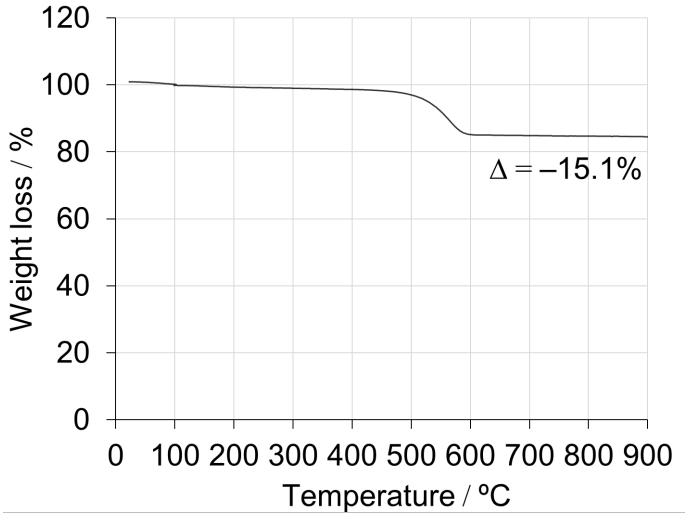

Figure S3. TG profile of the NPC/γ−alumina (SBa-200) composite under a steady flow of synthetic air, showing 15.1% of decrease at 650 ºC.

The number of the graphene layers n_{gra} was estimated using the gravimetric surface area of graphene S_{gra}, gravimetric surface area of a template S_{templ}, an experimentally obtained weight ratio of carbon deposited onto the surface of a template w_{exp}, and the theoretical weight ratio of single-layered carbon w_{gra} as,[S1]

$$w_{gra} = \frac{\left(\frac{S_{gra}}{2}\right)^{-1}}{S_{templ}^{-1} + \left(\frac{S_{gra}}{2}\right)^{-1}} \qquad \text{(S3)}$$

$$n_{gra} = \frac{w_{exp}}{w_{gra}} \qquad \text{(S4)}$$

Eq. S3 gave w_{gra} = 13.4 wt% for γ-Al_2O_3 (SBa-200) by using $S_{templ} = S_{BET}$ =203 m^2 g^{-1} from N_2 physisorption experiment, and S_{gra} =2627 m^2 g^{-1} evaluated by assuming that the carbons in graphene are planarly arranged as hexagons and that the C=C bond length is 0.142 nm. The resultant value of w_{gra} is in agreement with that from N_2 physisorption (15.1 wt%, Figure S3). n_{gra} was finally calculated to be 1.1 for NPC/NPG synthesized using γ-Al_2O_3 (SBa-200) from Eq. S4.

Raman Spectroscopy

Table S1. Assignments, peak positions ε_i, Lorentzian linewidths in HWHM Γ_i, and phonon lifetime τ_i for **NPC**s and **NPG**s synthesized with θ- and γ-Al_2O_3. τ_i was estimated by $\tau_i = \hbar/\Gamma_i$.

Entry	Assignment	ε_i /cm^{-1}	Γ_i /cm^{-1}	τ_i /fs	Entry	Assignment	ε_i /cm^{-1}	Γ_i /cm^{-1}	τ_i /fs
NPC	SW	1163	86	62	**NPC**	SW	1170	47	113
(θ-Al_2O_3)	D	1328	32	168	(γ-Al_2O_3)	D	1337	25	211
	G	1577	31	171		G	1589	24	221
	D'	1603	13	406		D'	1617	10	532
	SW+D	2454	38	141		SW+D	2480	40	134
	Background[a]	2634	359	15		Background	---	---	---
	G'	2651	56	95		G'	2659	47	113
	D+G	2909	58	91		D+G	2919	55	96
	2D'	3195	47	112		2D'	3208	58	91
NPG	SW	1113	52	102	**NPG**	SW	1122	42	127
(θ-Al_2O_3)	D	1330	21	257	(γ-Al_2O_3)	D	1338	16	322
	G	1575	22	239		G	1583	17	315
	D'	1611	12	436		D'	1619	8	658
	SW+D	2444	26	202		SW+D	2455	30	177
	G'	2653	35	150		G'	2663	31	174
	D+G	2914	40	134		D+G	2923	40	134

[a] The broad peak at 2634 cm^{-1} (Γ_i = 359 cm^{-1}) for **NPC** (θ-Al_2O_3) could be the remaining background which cannot be expressed by the polynomial background function.

We also measured the Raman spectrum of zeolite-templated carbon (ZTC) using Y-zeolite (ZTC (Y)) to rationalize the structure and defect density of **NPC**s as shown in Figure S4c. We found that ZTC (Y) contains highly defective graphitized domains. The G band at 1555 cm^{-1} and G' band at 2664 cm^{-1} (Table S2) reveals the existence of graphitized domains. The lack of the D' bands and broader line-widths of observed bands than those of **NPC**s (Table S1) suggest that the graphitized domains of ZTC (Y) is highly defective. The I_D/I_G = 0.74 results in the mean distance between defects in ZTC (Y) R_{ZTC} = 0.2 nm according to eq. (2) (Table 1). This matches well with λ_{Raman} = 1.1, which means every hexagonal ring has one defect and 45–65 times more defective than **NPC**s. Multiple defects as well as single defects exist in ZTC (Y). According to Eq. 4, only P_0 = 34% of hexagonal rings in ZTC (Y) remains non-defective while P_0 = 98% of hexagonal rings in **NPC**s are pristine. P_n (n = 1,2,3,4) of ZTC (Y) were calculated to be 36, 20, 7, and 2%, respectively, as shown in Figure 4. This defective nature of ZTC (Y) may come from the lower reaction temperature (800 °C) than those of **NPC**s (900 °C).

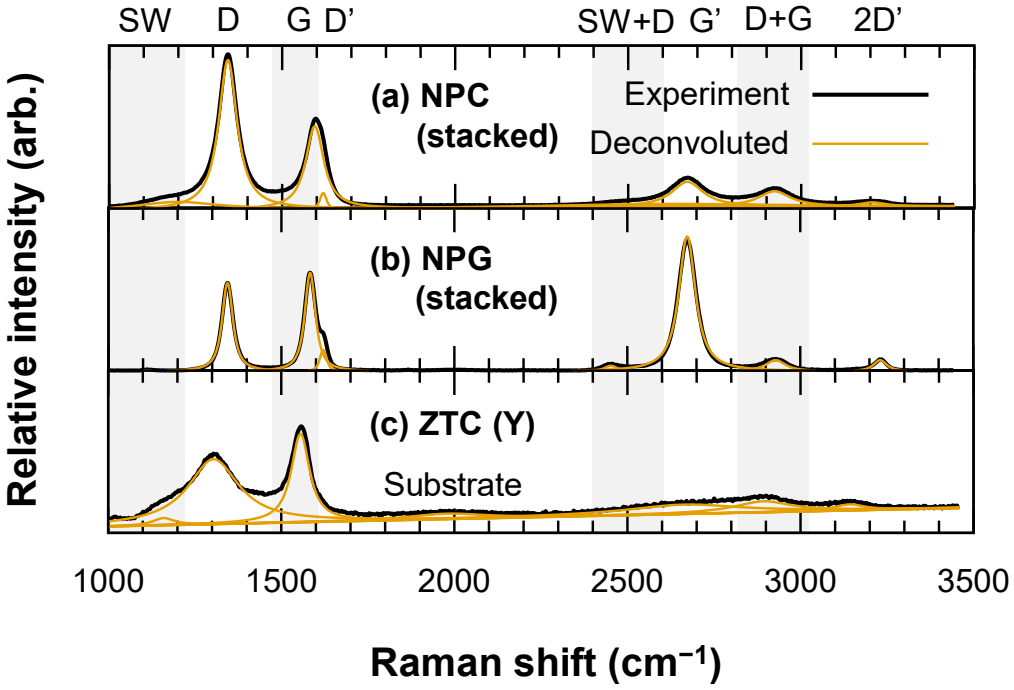

Figure S4. Experimental (black) and deconvoluted Raman spectra (with the polynomial background) of (a) **NPC** (stacked), (b) **NPG** (stacked), and (c) **ZTC** (Y). All measurements were performed at 2.33 eV (532 nm).

Table S2. Assignments, peak positions ε_i, Lorentzian linewidths in HWHM Γ_i, and phonon lifetime τ_i for **NPC** and **NPG**, and ZTC synthesized with the Y zeolite template. τ_i was estimated by $\tau_i = \hbar/\Gamma_i$.

Entry	Assignment	ε_i /cm^{-1}	Γ_i /cm^{-1}	τ_i /fs
NPC	SW	1195	148	36
(stacked)	D	1343	31	174
	G	1594	30	179
	D'	1619	7	789
	SW+D	2556	45	118
	Background[a]	2604	395	13
	G'	2671	54	98
	D+G	2923	56	95
	2D'	3206	46	116
NPG	SW	1113	52	102
(stacked)	D	1330	21	257
	G	1575	22	239
	D'	1611	12	436
	SW+D	2444	26	202
	G'	2653	35	150
	D+G	2914	40	134
	2D'	3222	27	200
ZTC	SW	1160	38	36
(Y-zeolite)	D	1304	89	88
	G	1555	32	30
	Substrate	1980	162	134
	G'	2664	181	200
	D+G	2893	207	100
	2D'	3142	52	53

[a] The broad peak at 2604 cm^{-1} (Γ_i = 395 cm^{-1}) for **NPC** (stacked) could be the remaining background which cannot be expressed by the polynomial background function.

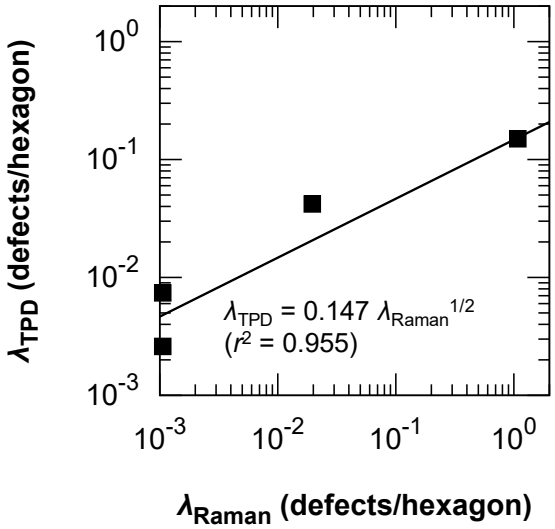

Figure S5. Correlation between λ_{Raman} and λ_{TPD} for a series of the porous carbon materials. r^2 represents correlation coefficient.

Transmission Electron Microscopy

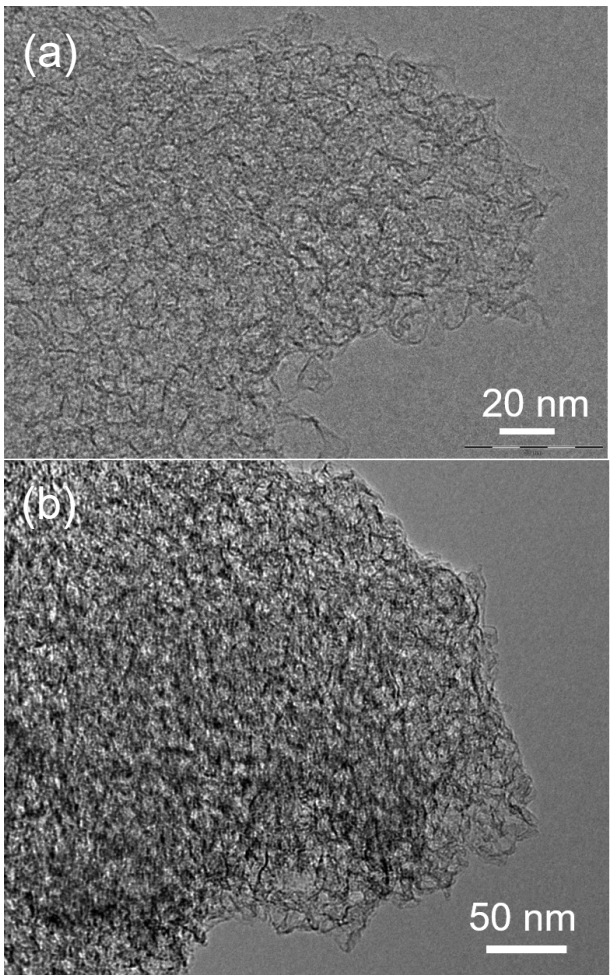

Figure S6. TEM images of **NPG**s synthesized using (a) θ-Al_2O_3 and (b) γ-Al_2O_3 as the templates.

References

S1. M. Yamamoto, S. Goto, R. Tang, K. Nomura, Y. Hayasaka, Y. Yoshioka, M. Ito, M. Morooka, H. Nishihara, T. Kyotani, *ACS Appl. Mater. Interfaces* **2021**, *13*, 38613–38622.

S2. T. Ishii, S. Kashihara, Y. Hoshikawa, J.-i. Ozaki, N. Kannari, K. Takai, T. Enoki, T. Kyotani, *Carbon* **2014**, *80*, 135-145.