Supporting Information

New Chemistry for New Material: Highly Dense Meso-Porous Carbon Electrode for Supercapacitors with High Areal Capacitance

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Characterization of 3D DMPC

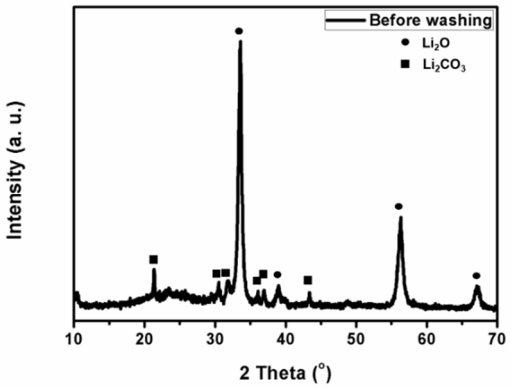

Figure S1. XRD pattern of products from Li and CO reaction before any treatment.

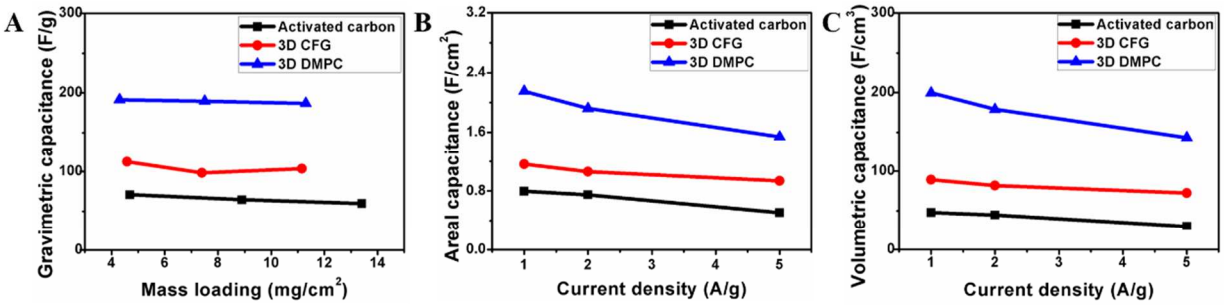

Figure S2. Electrochemical performance of activated carbon, 3D CFG, and 3D DMPC. (A) gravimetric capacitance with different mass loadings at current density of 1 A/g, (B) areal capacitance at different current densities, and (C) volumetric capacitance at different current densities.

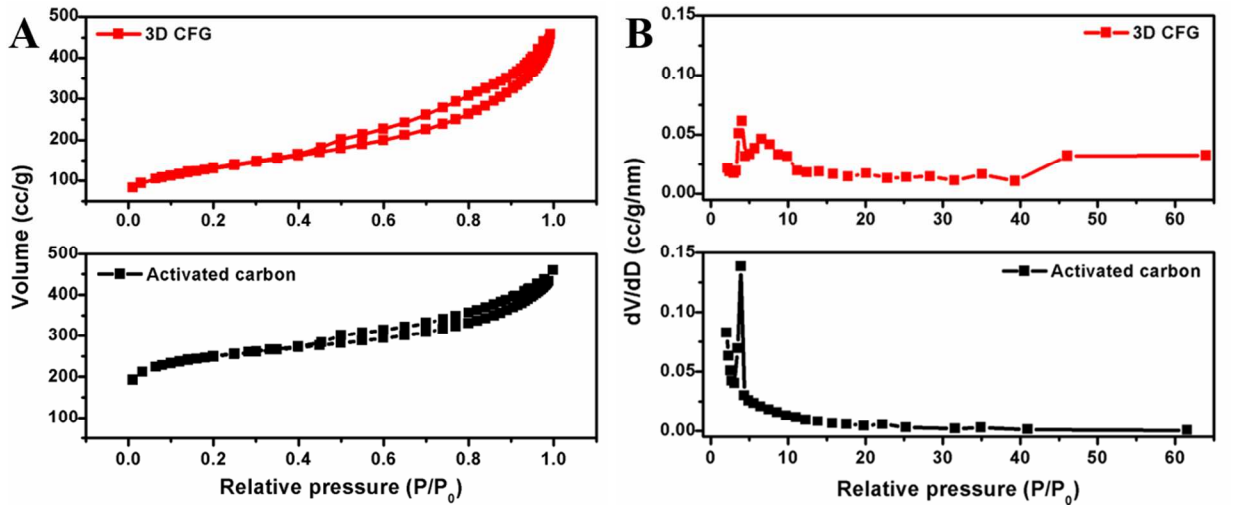

Figure S3. N_2 adsorption/desorption curves at 77 K (A) and corresponding pore size distribution (B) of activated carbon and 3D CFG.

Activated carbon (~100 mesh), purchased from Aldrich Chemical Company. Inc, possessed BET surface area of 853.5 m^2/g, in which micropore area contributed 500.3 m^2/g. Its pore sizes were concentrated on 4 nm. Whereas, 3D CFG synthesized from reaction between liquid Li and CO_2 gas at 550^{o}C for 48 h owned BET surface area of 462 m^2/g, in which microporous surface areas only occupied 70 m^2/g. Pore sizes focused on 2 to 70 nm.

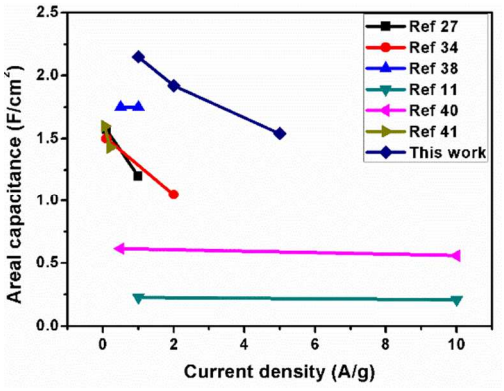

Figure S4. Comparison of areal capacitances between 3D DMPC and reported works.

Table S1. Areal capacitance of carbon-based EDLCs with aqueous electrolytes.

Electrode materials	Electrolyte	Mass loading	Current density	Gravimetric capacity	Volumetric capacity	Areal capacity	Ref
EM-CCG	1M H_2SO_4	10 mg/cm^2	0.1 A/g	157 F/g	255.5 F/cm^3	1.57 F/cm^2	27
			1 A/g	120 F/g	176 F/cm^3	1.20 F/cm^2	
Crumpled graphene balls	5M KOH	10 mg/cm^2	0.1A/g	150 F/g		1.5 F/cm^2	34
			2 A/g	105 F/g		1.05 F/cm^2	
3D graphene hydrogel	1M H_2SO_4/PVA	2 mg/cm^2	1 A/g	186 F/g		0.372 F/cm^2	35
3D porous carbon frameworks	6M KOH+PVA	10 mg/cm^2	0.5A/g	175 F/g		1.75 F/cm^2	38
			1 A/g	175 F/g		1.75 F/cm^2	
Carbon nanowebs	1M Na_2SO_4		2.5 mA/cm^2			973.5 mF/cm^2	39
			10 mA/cm^2			477.5 mF/cm^2	
2D porous carbon nanosheets	6M KOH	1 mg/cm^2	1A/g	228 F/g		0.227 F/cm^2	11
			10 A/g	210 F/g		0.210 F/cm^2	
Activated carbon fibers	1M H_2SO_4	2.1~2.5 mg/cm^2	0.5 A/g	247 F/g		0.617 F/cm^2	40
			10 A/g	227 F/g		0.56 F/cm^2	
3D hollow porous graphene balls	6M KOH	5 mg/cm^2	0.05A/g	321 F/g	134.8 F/cm^3	1.6 F/cm^2	41
			0.2 A/g	286 f/g	120.1 F/cm^3	1.43 F/cm^2	
3D dense mesoporous carbon	2M KOH	11.5 mg/cm^2	1 A/g	186.8 F/g	220.5 F/cm^3	2.15 F/cm^2	This work
			5 A/g	134 F/g		1.54 F/cm^2	

Note: The comparison was confined with aqueous electric double-layer capacitors with non-carbon based current collectors.

Synthesis Temperature Effects of 3D Dense Meso-porous Carbon (DMPC)

The synthesis temperature effect of 3D dense meso-porous carbon (DMPC) was evaluated using 450, 500, and 550^{o}C for 24 h. As shown in Figure S5, although FESEM images indicates the porous structure of 3 materials, reaction temperature clearly affected their pore size distributions. DMPC synthesized at 450^{o}C possesses thin pore walls and uniform nano-pores of less than 40 nm (Figure S5A and B). When 500^{o}C was used for the material synthesis, its pore

size increased to 40~80 nm with thicker pore walls (Figure S5C and D). As the reaction temperature increased to 550^{o}C, the uniform nano-pores disappeared and large microscale pores emerged (Figure S5E and F). The graphene layers of DMPC samples, which were determined from (002) planes of XRD pattern (Figure S6B), increased with increasing synthesis temperature, namely, the numbers of layers are 2, 3 and 4 for the samples prepared at 450, 500, and 550^{o}C, respectively. In contrast, the increase of synthesis temperature decreased the BET surface area (921, 857, and 372 m^2/g for samples prepared at 450, 500, and 550^{o}C, respectively). The relative small pores, which were observed from FESEM images, are further confirmed by pore size distribution curves obtained from N_2 adsorption using BJH model. Figure S6A shows narrow pore size distributions with average pore sizes of 5 and 6 nm for samples prepared at 450 and 500^{o}C, whereas the sample prepared at 550^{o}C possesses a wide pore size distribution between 2 and 30 nm. Raman spectra were exploited to evaluate defects and functional groups. Figure S6C shows D-band at 1350 cm^{-1}, which is attributed to sp^3 carbon atoms associated with defects and functional groups in graphene sheets, and G-band at 1580 cm^{-1}, which is due to sp^2 carbon atoms in the perfect structure of a graphene sheet. The intensity ratio of D-band and G-band indicated the content of sp^3 and sp^2 atoms, which is 1.14, 1.03 and 1.01 for samples prepared at 450, 500, and 550^{o}C, respectively. This indicates that the content sp^2 carbon atoms increases with increasing temperature. Furthermore, the functional groups were also examined by FTIR. As shown in Figure S6D, one can see the IR bands at 1065, 1225, 1400, and 1576 cm^{-1} corresponded to C-O, C-O-C, C-OH, and C=C vibrations, respectively.

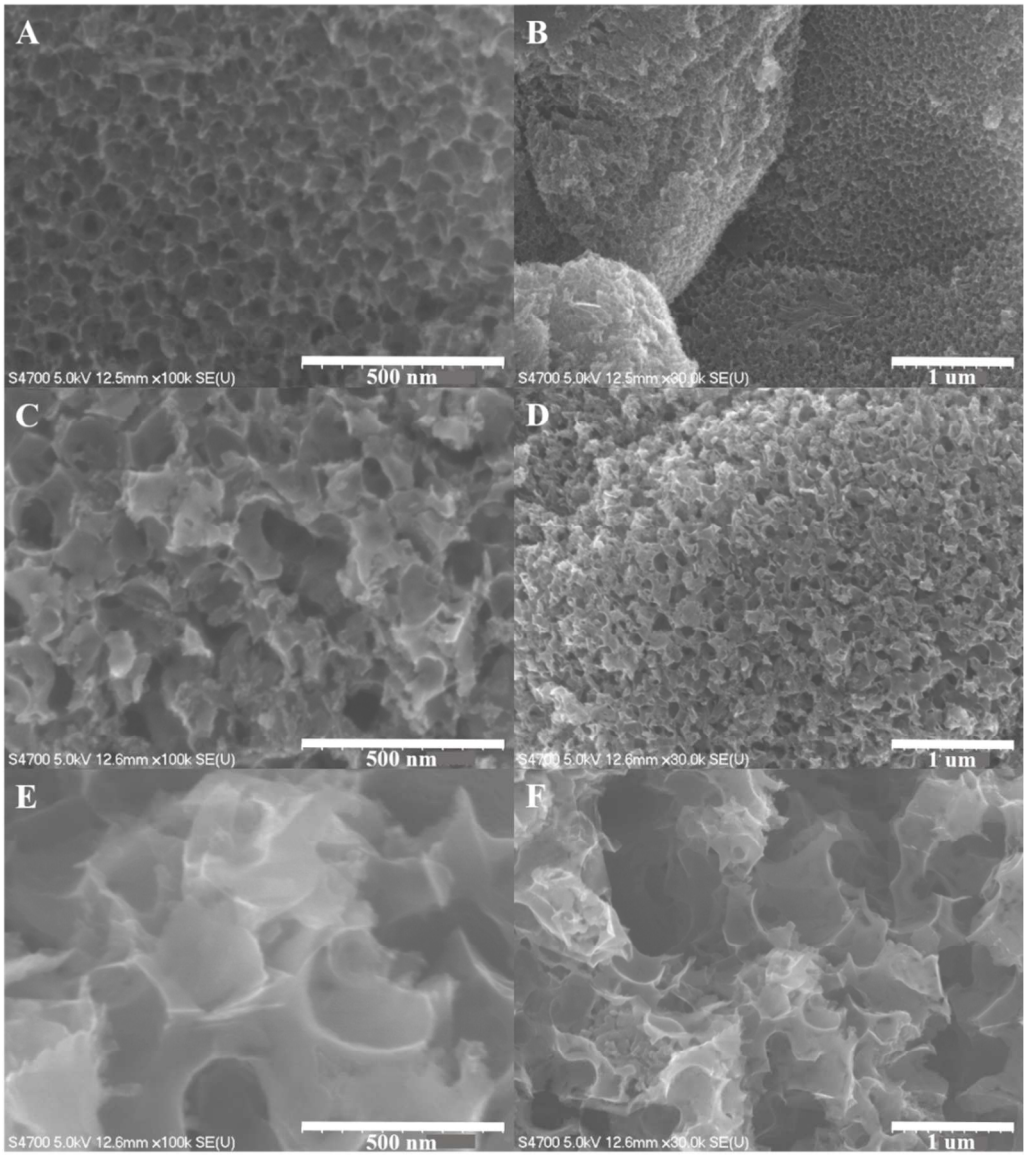

Figure S5. SEM images of 3D dense meso-porous carbon (DMPC). Samples synthesized for 24 hours at 450^{o}C (A, B), 500^{o}C (C, D), and 550^{o}C (E, F).

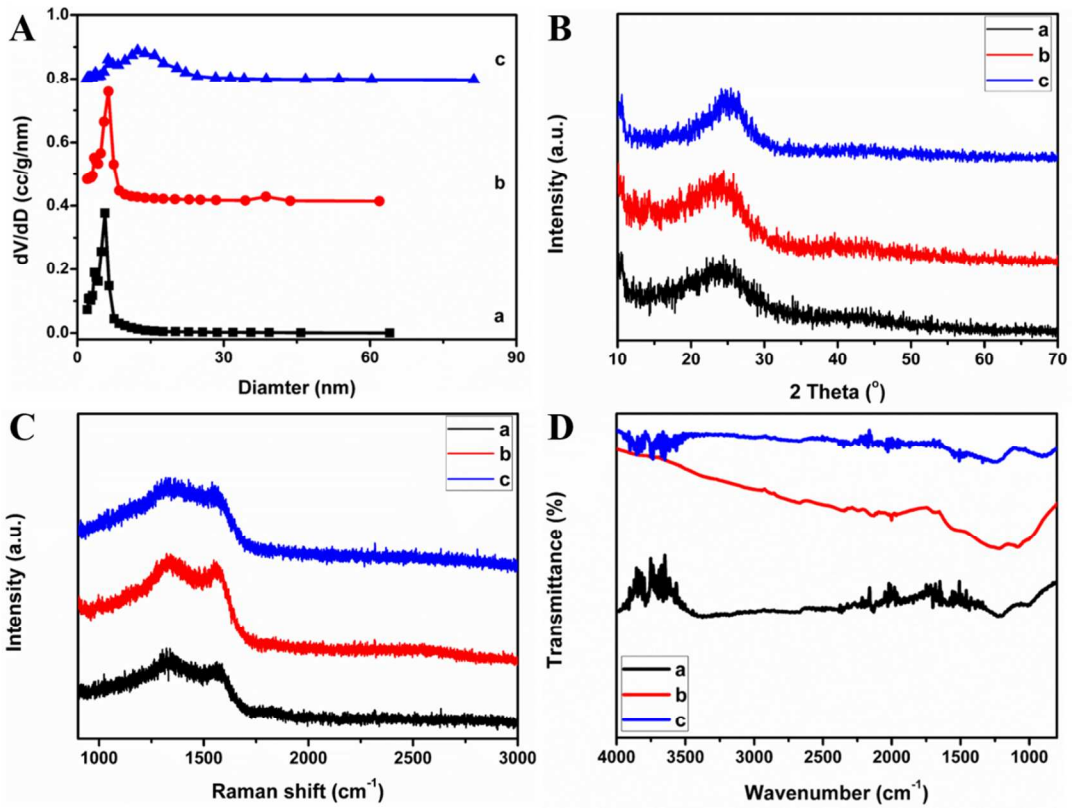

Figure S6. Characterization of 3D dense meso-porous carbon (DMPC) samples synthesized for 24 hours at 450°C (*a*), 500°C (*b*), and 550°C (*c*). (A) pore distribution, (B) XRD patterns, (C) Raman spectra, and (D) FTIR spectra.

To examine the synthesis temperature effects of DMPC on its electrochemical performance, a two-electrode configuration was employed to evaluate the electrochemical performance of DMPC samples prepared at 450, 500, and 550°C. As shown in Figure S7A and B, DMCP sample prepared at 500°C exhibited the best performance due to largest CV area and longest discharge time in CV at scan rate of 100 mV/s and galvanostatic charge/discharge cycles at current density of 1 A/g. Even when the current densities increased to 10 A/g, its specific capacitance is still 152 F/g, which is significantly larger than 92 and 62 F/g for DMPC samples prepared at 450 and 550°C, respectively. The excellent electrochemical performance of DMPC sample prepared at

500°C may be attributed to its 3D interconnected pore structure, large surface areas, and suitable functional groups. To further understand the capacitive performance, electrochemical impedance spectroscopy (EIS) tests were conducted. The intercept on the x-axis at a high frequency are associated with ohmic internal resistance, while the semicircles diameter from high to mid-frequency is related to charge transfer resistance, and the straight line at low frequency region represents ion diffusion resistance. Among three samples, the DMPC prepared at 500°C (which exhibited the highest capacitances) possessed smallest ohmic internal resistance, mediate charge resistance and ion diffusion resistance.

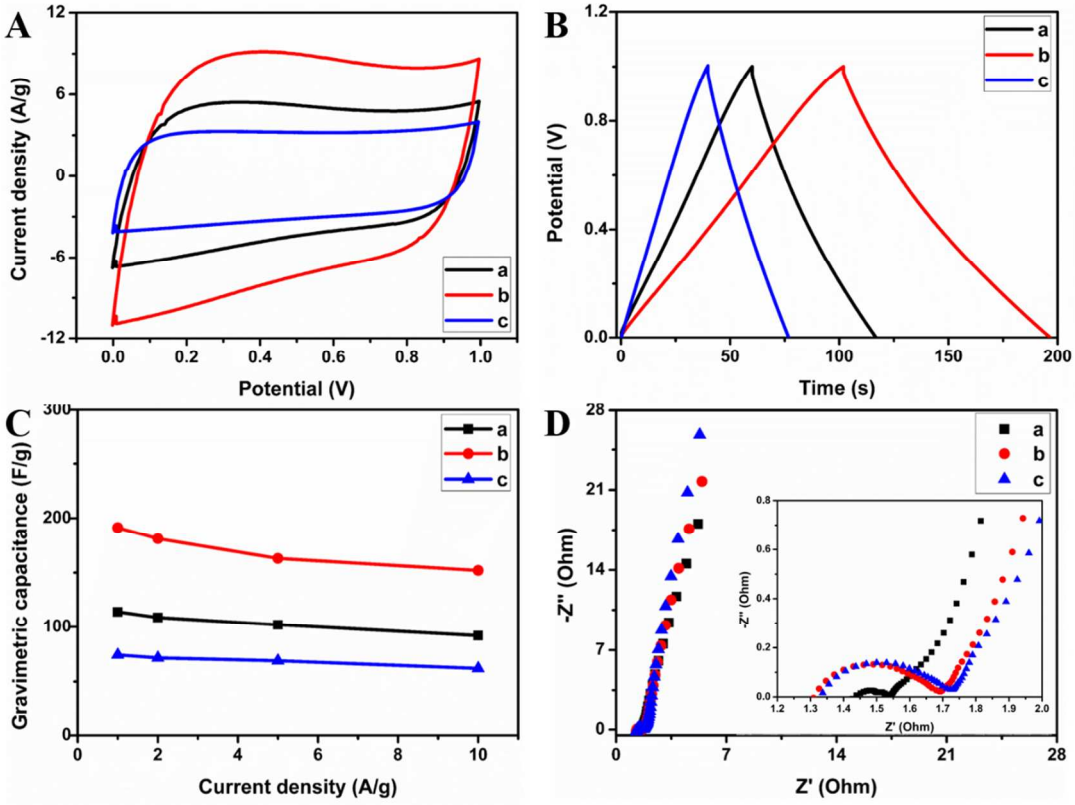

Figure S7. Electrochemical performance of 3D dense meso-porous carbon (DMPC) samples synthesized for 24 hours at 450°C (*a*), 500°C (*b*), and 550°C (*c*). (A) CV curves at scan rate of 100 mV/s, (B) galvanostatic charge/discharge profile at current density of 1 A/g, (C) current densities vs. specific capacitances, and (D) Nyquist plot with 0.01~10^5 frequencies.

Synthesis Time Effect of 3D Dense Meso-porous Carbon (DMPC)

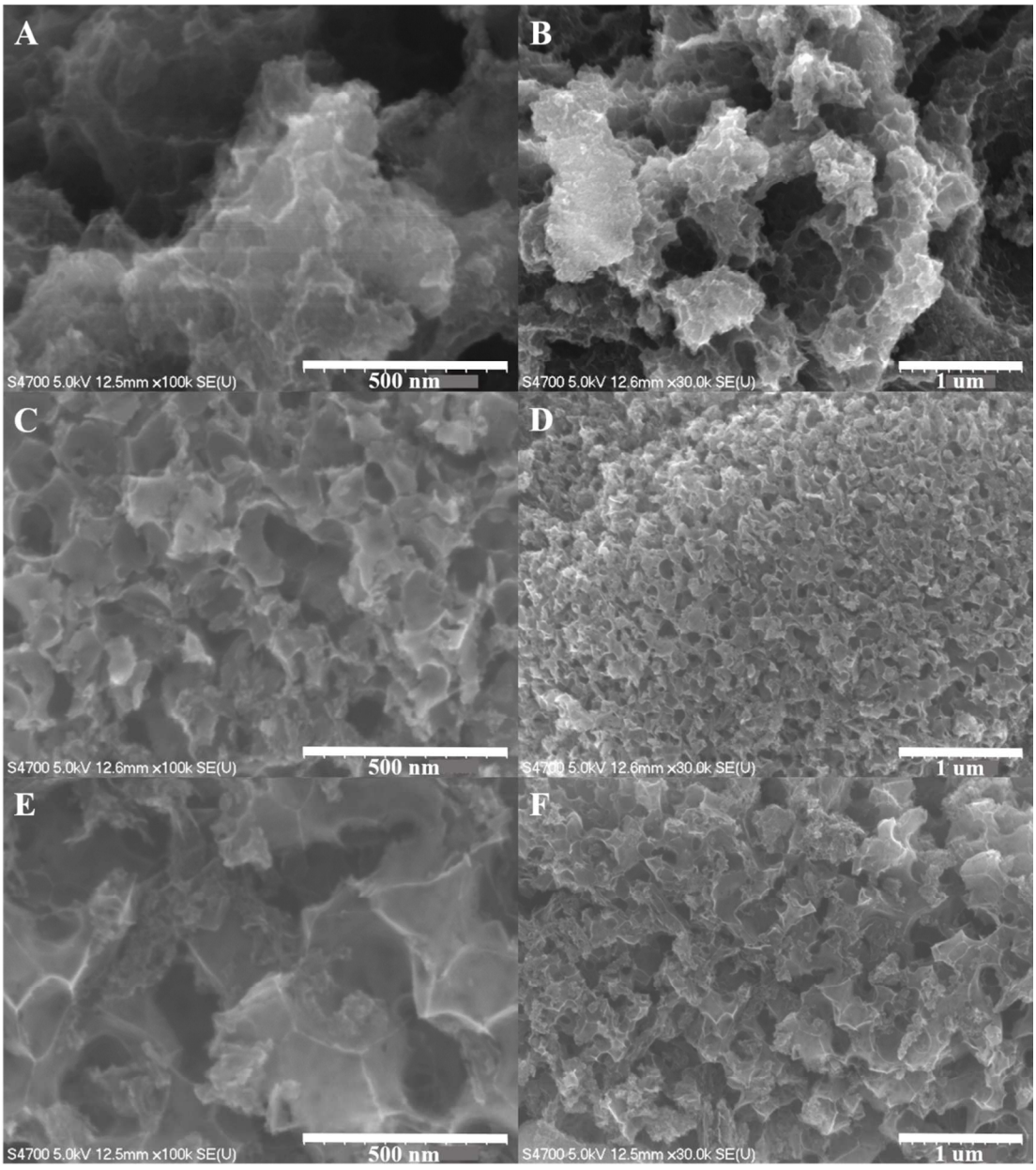

Figure S8. SEM images of 3D dense meso-porous carbon (DMPC). Samples synthesized at 500^{o}C for 12 hours (A, B), 24 hours (C, D), and 48 hours (E, F).

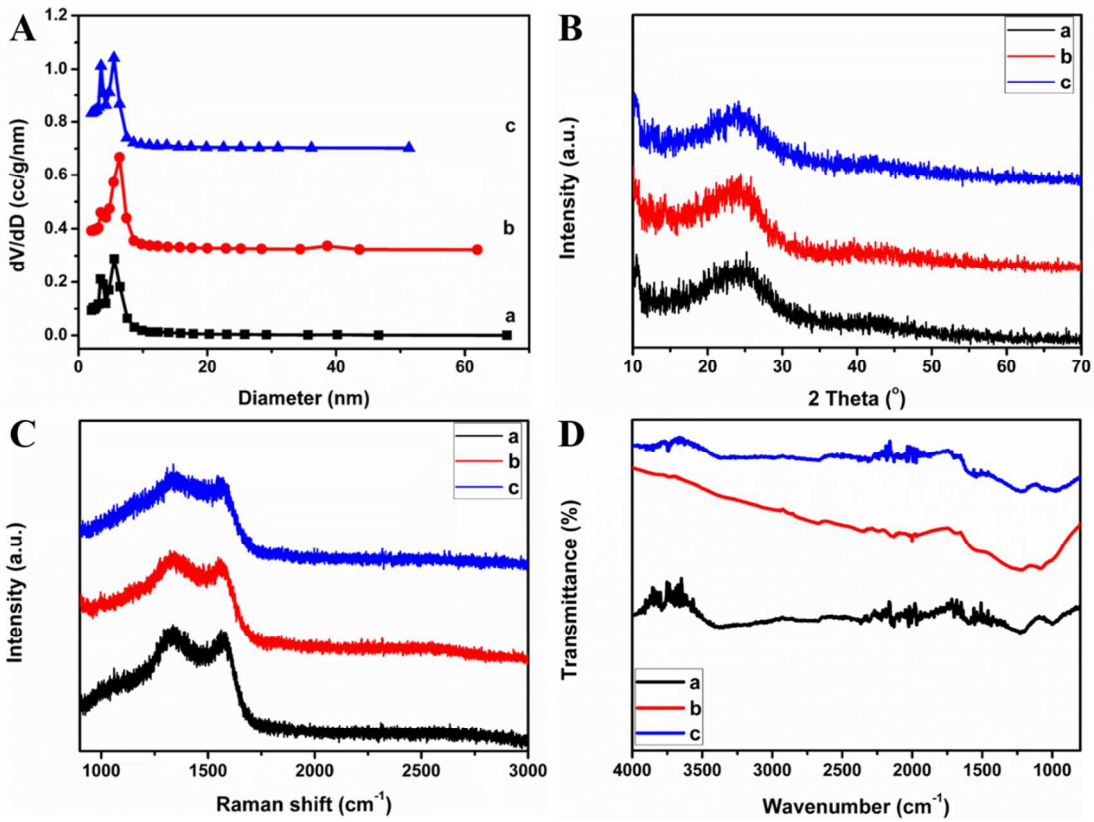

Figure S9. Characterization of 3D dense meso-porous carbon (DMPC) samples synthesized at 500°C for 12 hours (*a*), 24 hours (*b*), and 48 hours (*c*). (A) pore distribution, (B) XRD patterns, (C) Raman spectra, and (D) FTIR spectra.

Three times (12, 24, and 48 h) for DMPC synthesis at 500°C were employed to evaluate the time effect on its structure and properties and its capacitive performance. As shown in Figure S8A and B, DMPC sample prepared with 12 hours possesses small porous carbon clusters, which can be linked together to form a 3D interconnected framework by extending reaction time to 24 h (Figure S8C and D) and 48 h (Figure S8E and F). Each wall of all three samples contains 3 graphene layers, which was determined from (002) planes of XRD pattern (Figure S9B). The BET surface area, which was measured by N_2 adsorption at liquid nitrogen temperature, are 856, 857, and 984 m^2/g for samples prepared with 12, 24, and 48 hours, respectively (Figure S9A). As

shown by Raman spectra in Figure S9C, one can see similar ratios of sp^3 and sp^2 carbon atoms, which are based on relative intensity of D-band (sp^3 carbon atoms) at 1350 $cm^{-1}$and G-band (sp^2 carbon atoms) at 1580 cm^{-1} for all three samples. The functional groups in those samples are C-O, C-O-C, C-OH, and C=C with IR bands at 1065 cm^{-1}, 1225 cm^{-1}, 1400 cm^{-1} and 1576 cm^{-1}, respectively (Figure S9D)

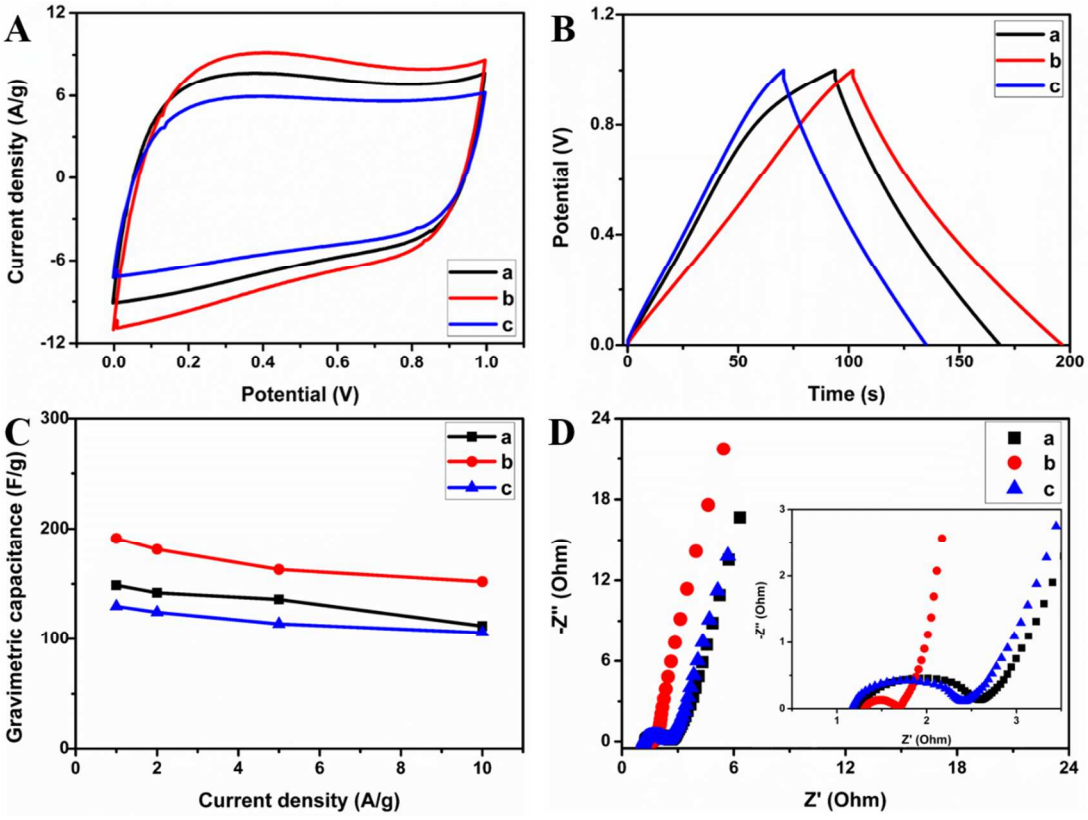

Figure S10. Electrochemical performance of 3D dense meso-porous carbon (DMPC) samples synthesized at 500°C for 12 hours (*a*), 24 hours (*b*), and 48 hours (*c*). (A) CV curves at scan rate of 100 mV/s, (B) galvanostatic charge/discharge profiles at current density of 1 A/g, (C) current densities vs. specific capacitances, and (D) Nyquist plot with 0.01~10^5 frequencies.

The electrochemical performance of those three DMPC samples, which were respectively prepared at 500°C for 12, 24, and 48 hours, was evaluated with CV at scan rate of 100 mV/s and galvanostatic charge/discharge cycles at current density of 1 A/g. The electrode of DMPC sample prepared with 24 hours exhibited the largest CV area (Figure S10A) and longest discharge time (Figure S10B), indicating the best charge accumulation and largest energy storage among three samples. This was further supported by the calculated gravimetric capacitances, namely, 148.8, 191.4, and 129.8 F/g for DMPC samples prepared with 12, 24, and 48 hours, respectively. Even when the current density increased to 10 A/g, the DMPC prepared with 24 hours can still keep the best performance with capacitance of 152 F/g. The excellent electrochemical performance is due to its smallest charge transfer resistance and ion diffusion resistance, which are revealed its electrochemical impedance spectroscopy (Figure S10D).

Electrochemical performance of DMPC at mass loading of 14.72 mg/cm^2 in three-electrode configuration.

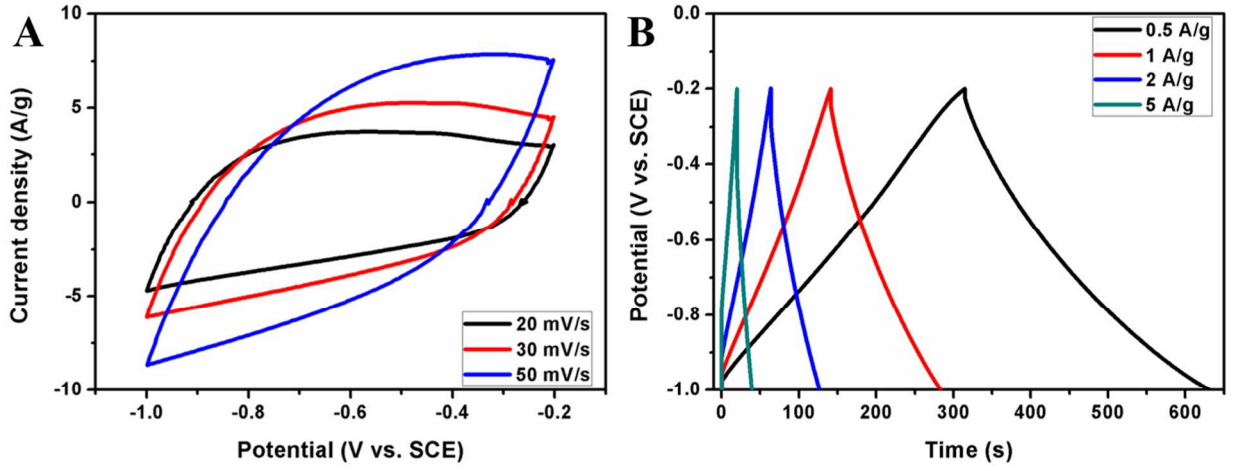

Figure S11. Electrochemical performance of DMPC at mass loading of 14.72 mg/cm^2. (A) CV curves at scan rates of 20~50 mV/s and galvanostatic charge/discharge profiles at current densities of 0.5~5 A/g.

The electrochemical performance of DMPC at mass loading of 14.72 mg/cm^2 was tested in 2M KOH aqueous solution with three-electrode configuration. At such a large mass loading, DMPC possessed CV curves with slight polarization and GCD profiles with small IR drop. The specific capacitance can be 198.6, 178.8, 159.7, and 125 F/g at 0.5, 1, 2, and 5 A/g, respectively.