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Supporting Information

Adsorption dominant sodium storage in three-dimensional coal-based graphite microcrystal/graphene composites

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Table S1 The component analysis of anthracite.

Proximate analysis/wt%				Ultimate analysis [a]/wt%				
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C	H	O	N	S
4.28	24.87	1.05	69.80	68.10	0.67	0.84	0.93	0.31

Note: M_{ad}: Moisture content; A_{ad}: Ash content; V_{ad}: Volatile matter content; FC_{ad}: Fixed carbon content. a): The ultimate analysis test of coal was based on air dry basis.

Table S2 Physical parameter of as-prepared samples

Sample	**graphene**	**3D-CGC/G0.5**	**3D-CGC/G1**	**3D-CGC/G2**	**CGC**
d_{002}（Å）	3.71	3.56	3.50	3.47	3.40
I_D/I_G [a]	1.34	1.40	1.58	1.74	2.39
SSA N_2 [b] (m^2/g)	88.79	29.93	26.57	15.55	11.81
V_t N_2 [c] (cm^3/g)	0.365	0.174	0.156	0.099	0.033

[a] The value of I_D/I_G is the integral intensity ratio of fitting D band and G band peaks;

[b] The specific surface area (SSA) was tested by N_2 absorption apparatus.

[c] The total pore volume was determined by N_2 adsorption.

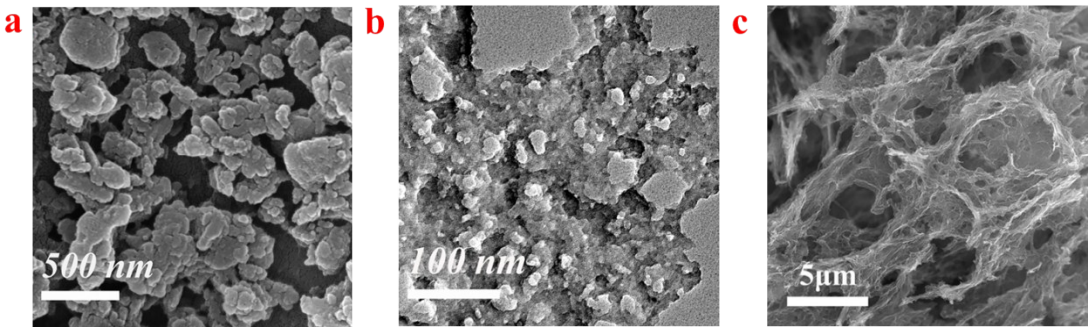

Figure S1 (a) SEM and (b) TEM images of CGC, and (c) the SEM image of graphene.

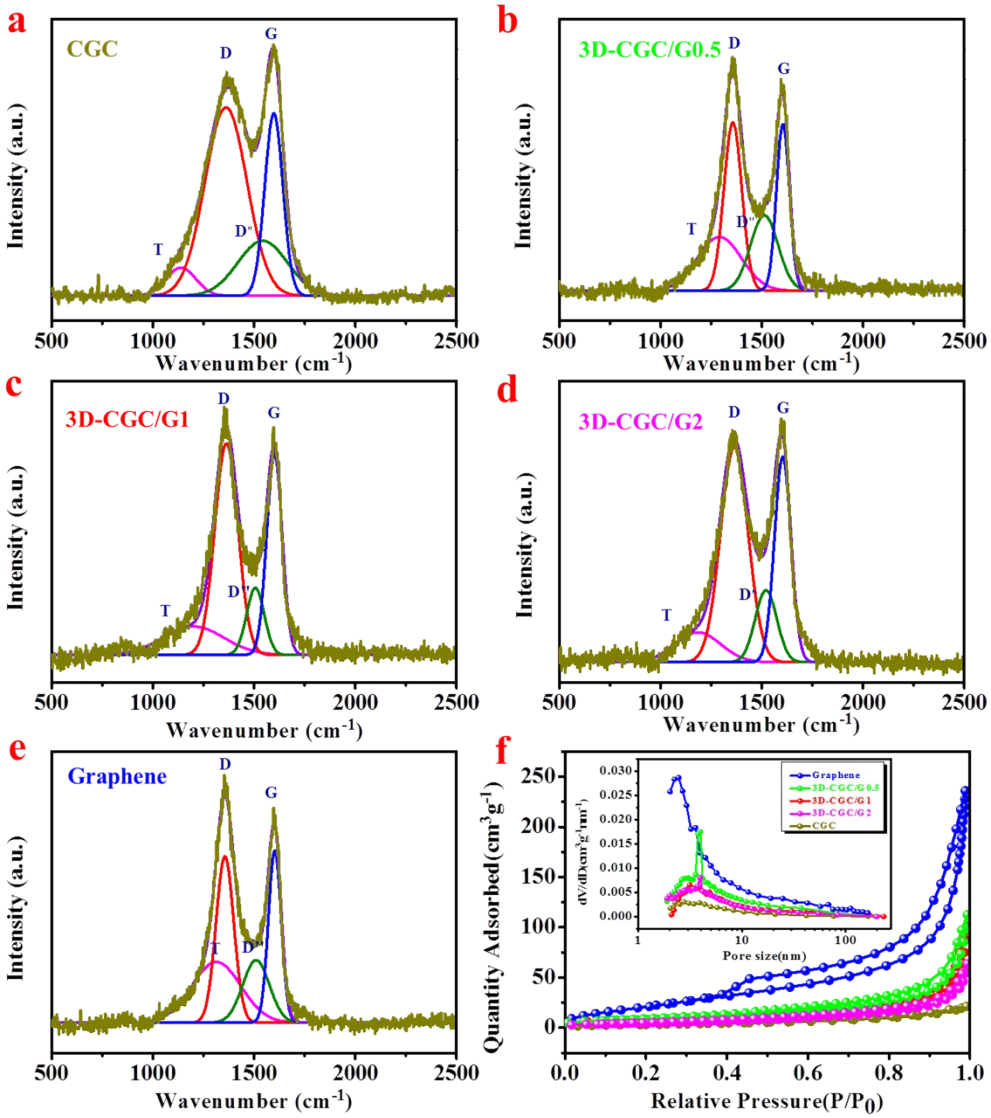

Figure S2 (a-e) Fitted Raman spectra of CGC, 3D-CGC/Gs and graphene; (f) Nitrogen adsorption/desorption isotherms and the corresponding BJH pore-size distribution curves (inset) of all samples.

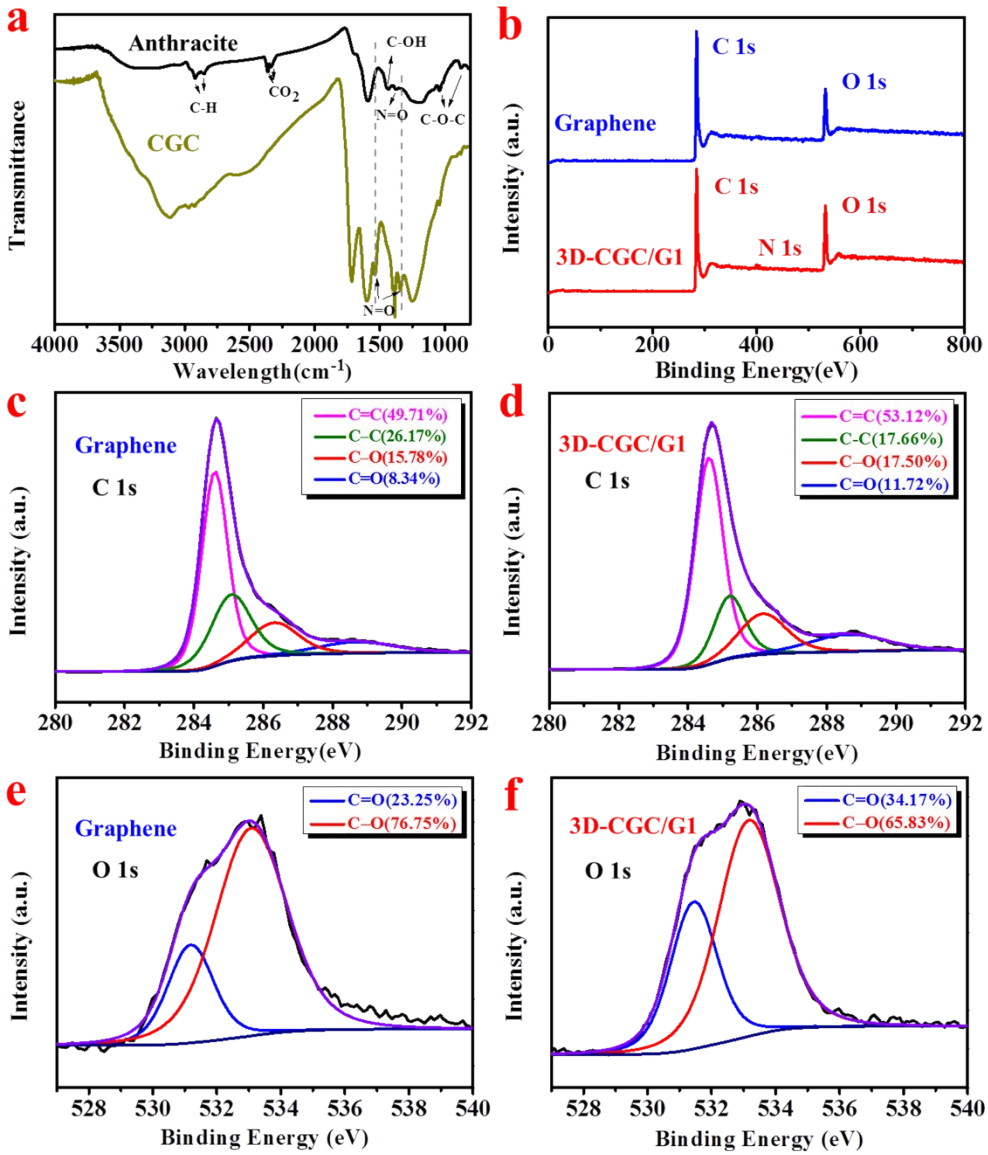

Figure S3 (a) FT-IR spectra of raw anthracite and CGC. (b) XPS survey spectra of graphene and 3D-CGC/G1; High-resolution C 1s of (c) graphene and (d) 3D-CGC/G1; and the O 1s spectra of (e) graphene and (f) 3D-CGC/G1.

The wide spectra of samples (Figure S3b) show three characteristic peak signals of C 1s, N 1s and O 1s, located at 284.6, 399.6 and 532.6 eV, without any other peak signals. The appearance of N elements is attributed to the HNO_3 treatment during the synthesis process, as also reflected by FT-IR. The high resolution C 1s profiles of all

two samples (Figure S3c-d) can be fitted into four peaks, assigned as C=C (284.6 eV), C–C (285.2±0.1 eV), C–O (286.2±0.1 eV) and C=O groups (288.5±0.1 eV), respectively [1], which demonstrate the existence of oxygen functional groups. For the high-resolution O 1s spectra (Figure S3e-f), the curves can be split into two curves, corresponding to C=O groups (531.3±0.1 eV) and C–O groups (533.1±0.1 eV) [2]. Notably, the content of C=O groups for 3D-CGC/G1 (34.17 %) is higher than graphene (23.25 %), which could provide much more reactive sites on carbon surface, enhancing capacitive properties [3, 4].

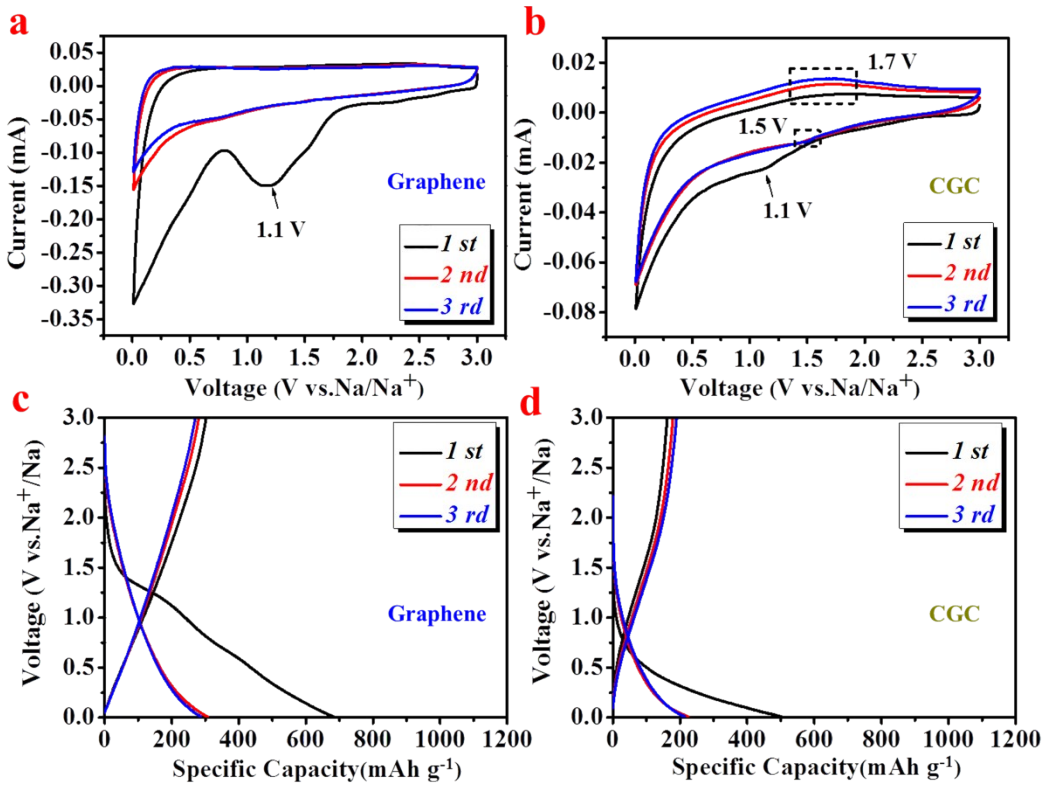

Figure S4 (a, b) The first three CV curves and (c, d) charge/discharge profiles of graphene and CGC.

The first three CV curves and charge/discharge profiles of graphene and CGC are

displayed in Figure S4. For graphene, one wide irreversible reduction peaks (at 1.1 V) in first CV curves (Figure S4a) was observed and vanished in subsequent cycles, which may ascribed to the decomposition of electrolyte, the formation of SEI film and the side reaction of surface functional groups. And the discharge voltage profile of it (Figure S4c) could be divided into two regions, which contains a soar-drop region (>1.5 V) and a slow sloping region (<1.5 V), corresponding to the capacitance behavior and adsorption of defects and functional groups on the surface of graphene sheets, respectively [5, 6]. For the initial CV profile of CGC (Figure S4b), only one irreversible reductive peak (at 1.1 V), related to the decomposition of electrolyte, formation of SEI film and the side reaction of surface functional groups, was revealed. And in the subsequent cycles, one pair of redox peaks at 1.5/1.7 V was observed, which can be ascribed to the redox reactions between Na^+ and oxygen functional groups [3, 7]. The charge/discharge curves for CGC also shows one sloping region, corresponding to the (de-)adsorption between Na^+ and surface functional groups and defects. Obviously, the sloping voltage profiles in different degree suggest that the adsorption dominates the Na^+ storage for all samples.

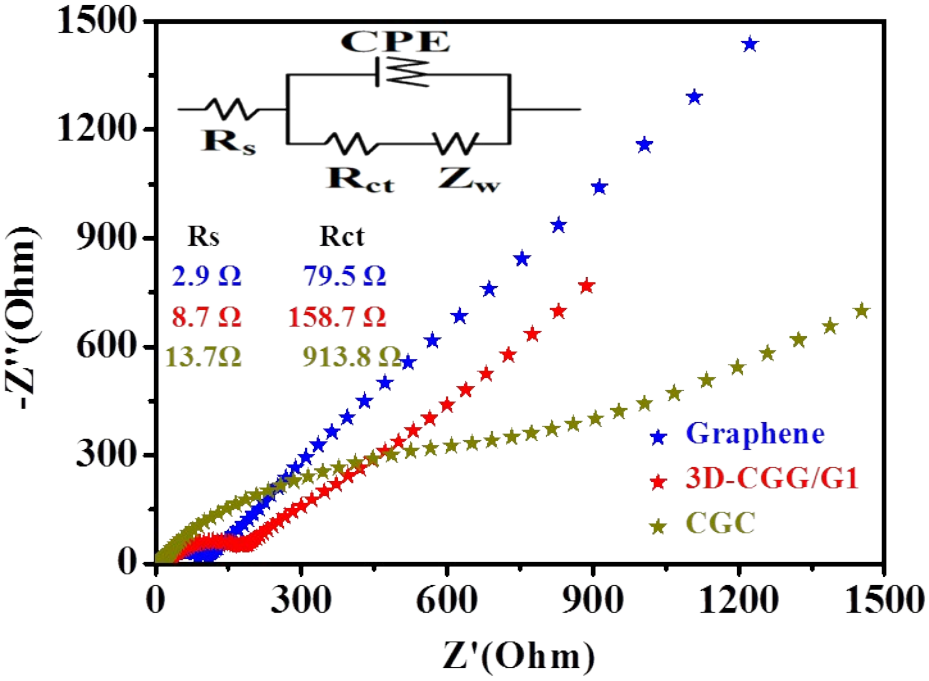

Figure S5 EIS spectra of the CGC, 3D-CGC/G1, and graphene anodes. The inset shows corresponding equivalent fitting circuit for the electrodes. R_s: the equivalent series resistance, including the interface contact impedance and the inherent impedance of the electrodes and electrolyte; R_{ct}: charge-transfer resistance; CPE: capacitance expressed by a constant phase element; Z_W: the Warburg impedance related to the ion diffusion.

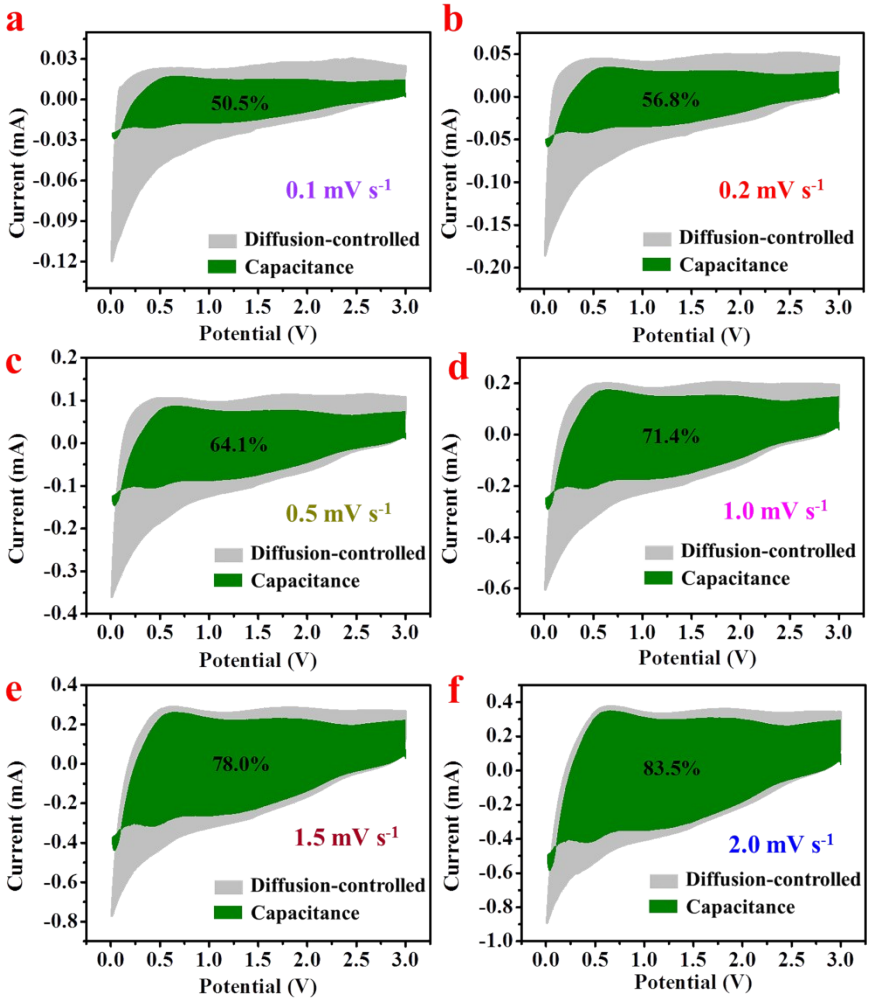

Figure S6 Capacitance contribution (green region) in 3D-CGC/G1 at (a) 0.1, (b) 0.2, (c) 0.5, (d) 1.0, (e) 1.5, (f) 2.0 mV s^{-1}.

Reference

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