Supporting Information

Three-Dimensional Double-Walled Ultrathin Graphite Tube Conductive Scaffold with Encapsulated Germanium Nanoparticles as a High-Areal-Capacity and Cycle-Stable Anode for Lithium-Ion Battery

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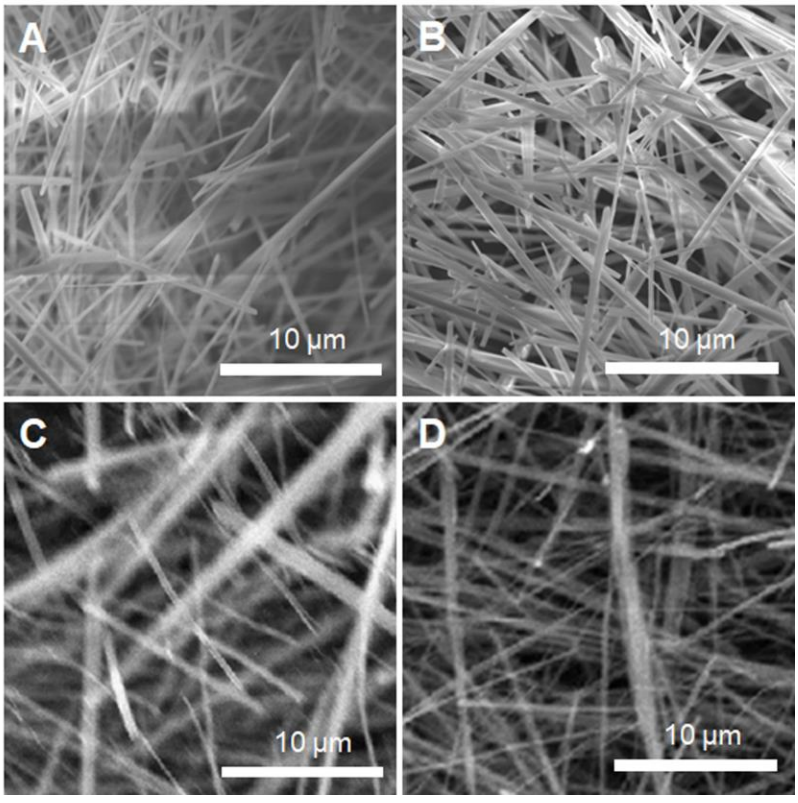
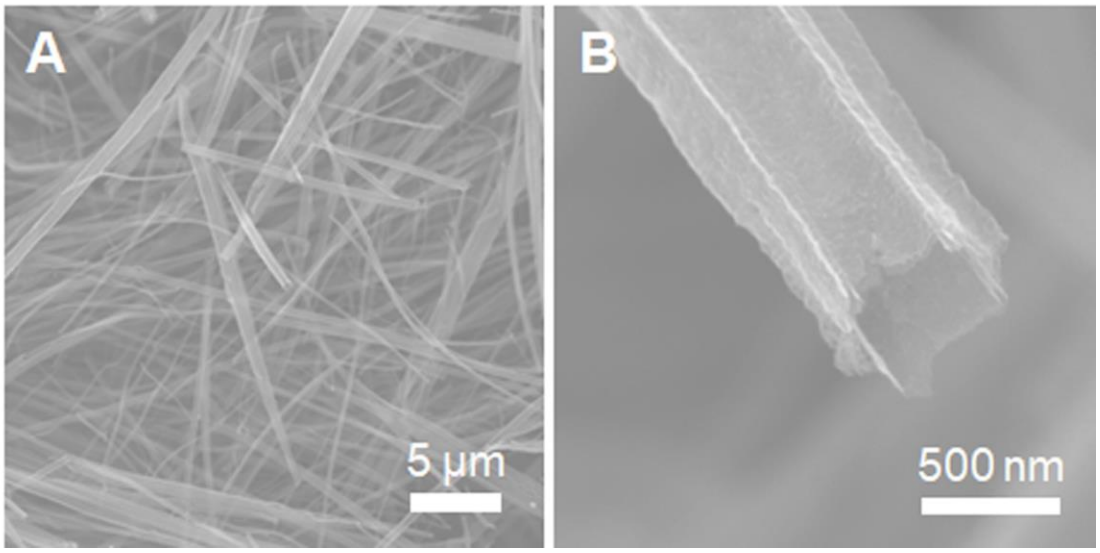
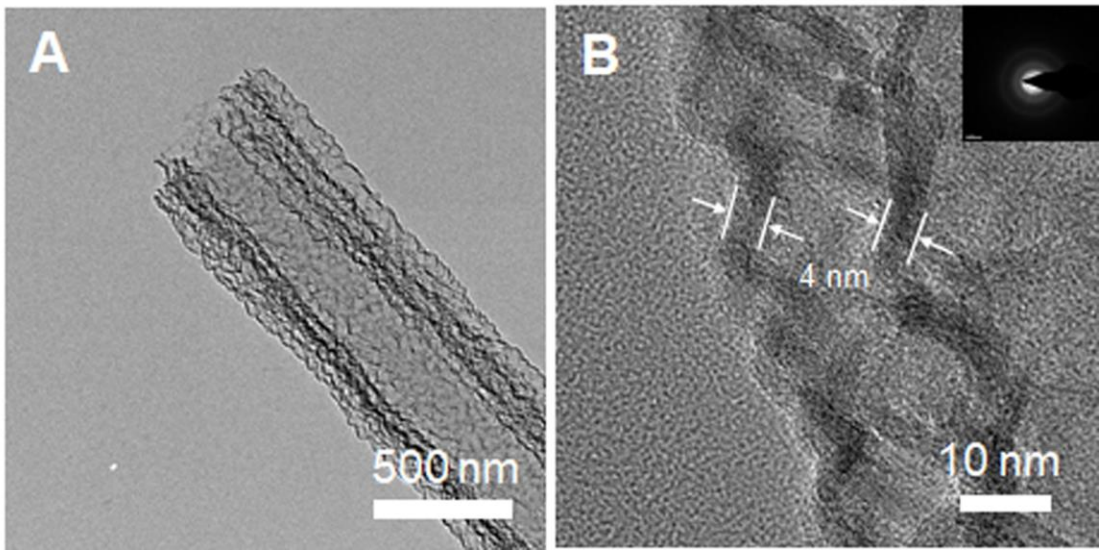


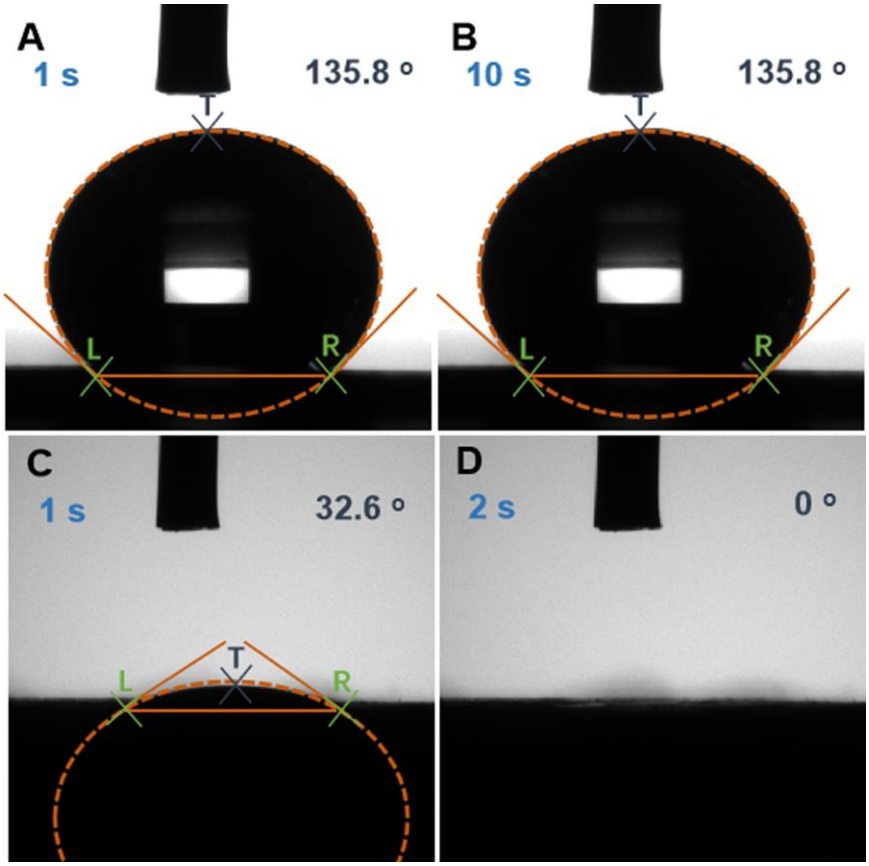
Supplementary Figure 1. (A) SEM image of the 3D-MgO rod. (B) SEM image of the 3D-MgO/N-doped graphene. (C) SEM image of the 3D-MgO/N-doped graphene/MgO. (D) SEM image of the 3D-MgO/N-doped graphene/MgO/graphene.



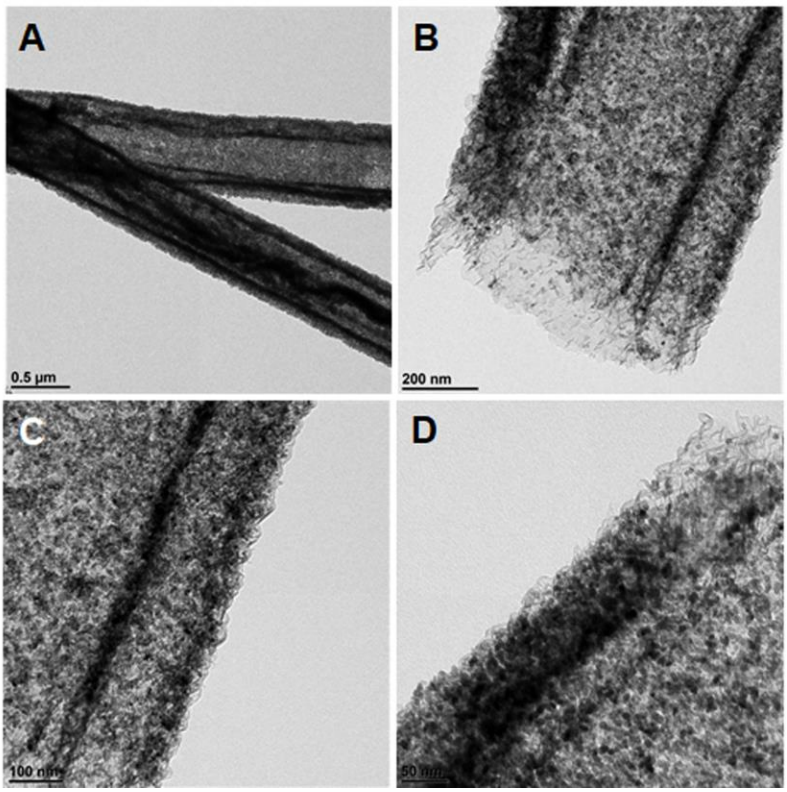
Supplementary Figure 2. Morphology characterization of the 3D-DHGT. (A,B) SEM images of the 3D-DHGT.



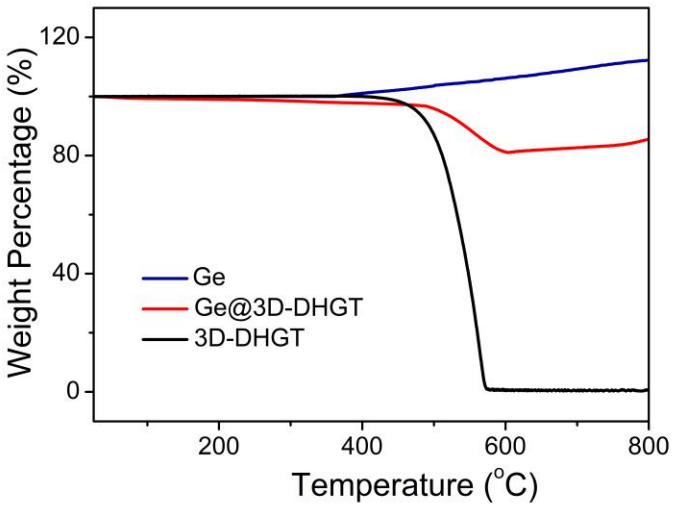
Supplementary Figure 3. (A,B) TEM images of the 3D-DHGT. The inset in (B) is the electronic diffraction pattern corresponding to the 3D-DHGT.



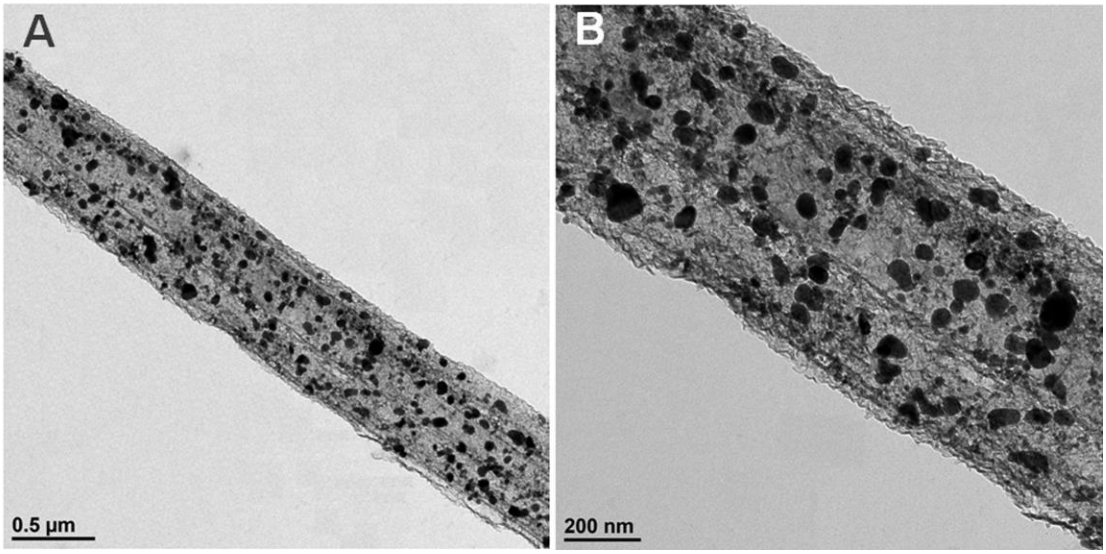
Supplementary Figure 4. (A-D) Variation of water CA over time (A,B) on the surfaces of outer graphene layer and (C,D) on the surfaces of inner N-doped graphene layer.



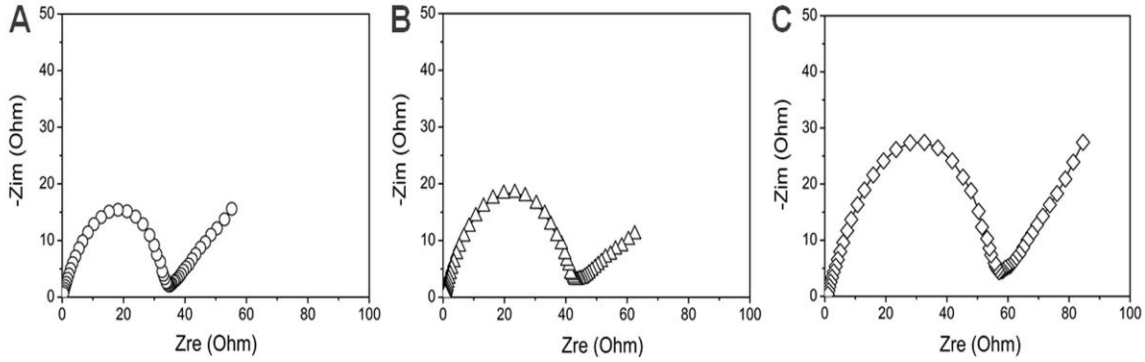
Supplementary Figure 5. (A-D) TEM images of the GeO_2@3D-DHGT.



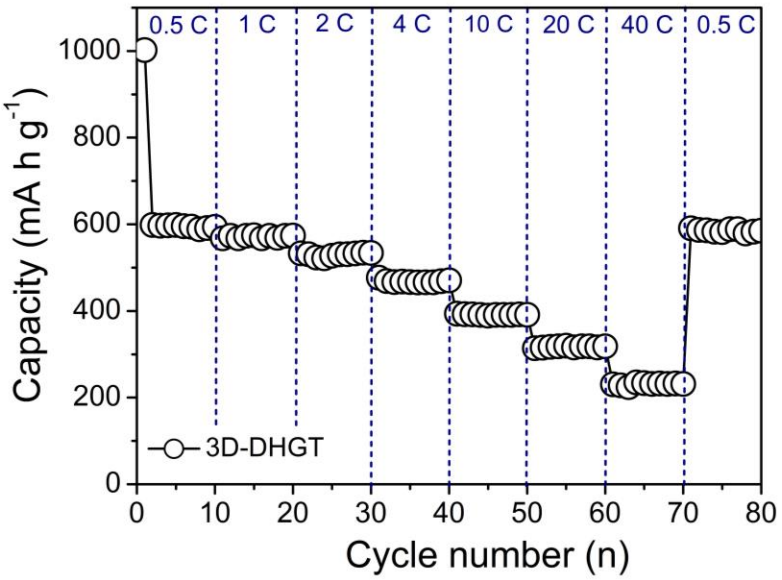
Supplementary Figure 6. TGA curves of Ge, 3D-DHGT, and Ge@3D-DHGT in air at a heating rate of 5 °C min^{-1}.



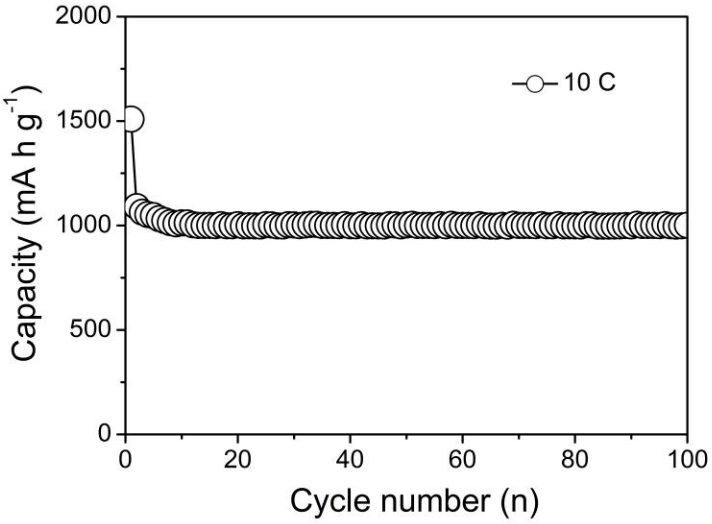
Supplementary Figure 7. TEM images of the Ge@3D-DHGT electrode after 1000 cycles at a rate of 0.5 C.



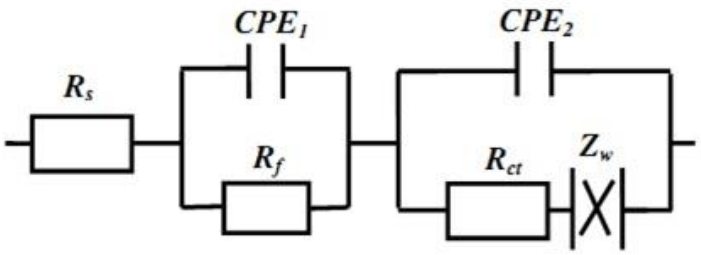
Supplementary Figure 8. Nyquist plots of Ge@3D-DHGT electrodes (a) before cycling, (b) after 100 cycles, and (c) after 1000 cycles.



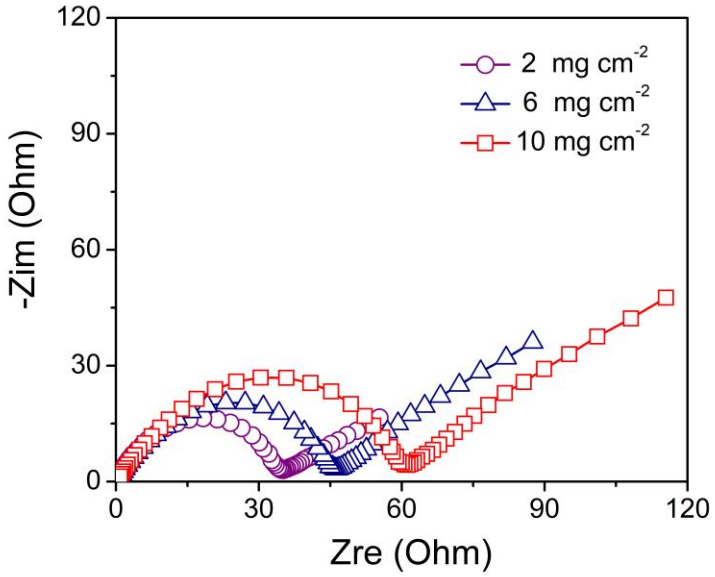
Supplementary Figure 9. Rate performance of the 3D-DHGT electrode at different current densities from 0.5 C to 40 C.



Supplementary Figure 10. Cycling performance (discharge) of Ge@3D-DHGT electrode with a mass loading of 2 mg cm^{-2} at 10 C for 100 cycles.



Supplementary Figure 11. The equivalent circuit for the impedance behavior of the electrode.



Supplementary Figure 12. Nyquist plots of Ge@3D-DHGT electrodes under different mass loadings (2 mg cm^{-2}, 6 mg cm^{-2}, and 10 mg cm^{-2}).

Supplementary Table S1. Mass ratio of Ge and 3D-DHGT at different temperature.

	3D-DHGT (wt%)	Ge (wt%)	Ge@3D-DHGT (wt%)	Ge:3D-DHGT (mass ratio)
600 °C	0.10	106.54	82.22	77.80: 22.20
625 °C	0.09	106.89	82.57	77.23:22.77
650 °C	0.06	107.67	82.93	77.01:22.99

700 °C	0.06	108.42	83.31	76.83:23.17

The residual weight percentage of 3D-DHGT, Ge, and the Ge@3D-DHGT at 600, 625, 650 and 675 °C are used to calculate the mass ratio of Ge and 3D-DHGT in the Ge@3D-DHGT composite. The weight of Ge increased during high temperature zone because the formation of GeO_X, meanwhile the weight of graphene decreased during the heat treatment owing to the decompose of graphene. Hence, we can use this equation to calculate the mass ratio of Ge and 3D-DHGT:

$$W_{3D\text{-}DHGT}(1-X_{Ge})+W_{Ge}X_{Ge}=W_{Ge@3D\text{-}DHGT}$$

Where $W_{3D\text{-}DHGT}$, W_{Ge}, $W_{Ge@3D\text{-}DHGT}$ are the residual weight percentage of 3D-DHGT, Ge and Ge@3D-DHGT at different temperature, respectively, X_{Ge} is the mass ratio of Ge in the composite. The mass ratio is listed in the table S1, which is quite stable at different temperature, and the average mass ratio of Ge and 3D-DHGT in the composite is 77.22% of Ge and 22.78% of 3D-DHGT.

Supplementary Table S2. A comparison of the cycle and rate performance of various Ge-based composites prepared by different structure designs.

Materials	Carbon black (%)	Mass loading (mg cm^{-2})	Low Current Rate (C)	Capacity (mA h g^{-1})	High Current Rate (C)	Capacity (mA h g^{-1})	Reference
3D Macroporous Ge Particle	10	1.08	0.2	1436	5	717	[1]
Mesoporous Ge Particles	15	NA	0.2	1350	5	804	[2]
Carbon-Encapsulated Ge Nanowires	5	NA	0.2	1428	10	792	[3]
Graphite Tubes-Encapsulated Ge Nanowires	20	0.5	0.15	1310	7	232	[4]
Ge-Graphene-Carbon Nanotube Composite	10	0.7	0.1	1277	2	754	[5]

Graphene-Coating Ge Nanowires	15	1.9	0.3	1300	20	363	[6]
Carbon Nanofibers-Encapsulated Ge Nanoparticles	0	0.5	0.15	1420	15	480	[7]
Flexible Carbon-Coated Ge Nanowires on Carbon Nanofibers	0	1.2	0.1	1400	10	484	[8]
Ge@C/rGO Hybrids	10	1	0.1	1258	20	712	[9]
N-Doped Carbon with Embedded Ge Nanoparticles	0	2.24	0.1	1450	15	803	[10]
Polycrystalline Ge Microwire Film	0	NA	0.1	1350	1	1000	[11]
Core-Shell Ge@ Graphene@TiO_2 Nanofibers	0	3.2	0.1	1150	2	760	[12]
Cu/Si/Ge NW Arrays Grown on Ni Foam	0	1.2	1	2373	16	1010	[13]
Nanoporous Ge Nanofibers	15	1	0.2	1200	30	200	[14]
Ge@3D-DHGT	**0**	**2**	**0.5**	**1338**	**40**	**752**	**This work**
		6		**1121**	**20**	**536**	
		10		**1001**	**20**	**345**	

Supplementary Table S3. Impedance parameters calculated from equivalent circuit.

	R_s (Ω)	R_f (Ω)	R_{ct}(Ω)
Ge/Cu	6	62	25
Ge@3D-DHGT	3	29	11

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