Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information

Binder-Free Germanium Nanoparticle decorated Multi-Wall Carbon Nanotube Anodes prepared via two-step Electrophoretic Deposition for high capacity Li-Ion Batteries

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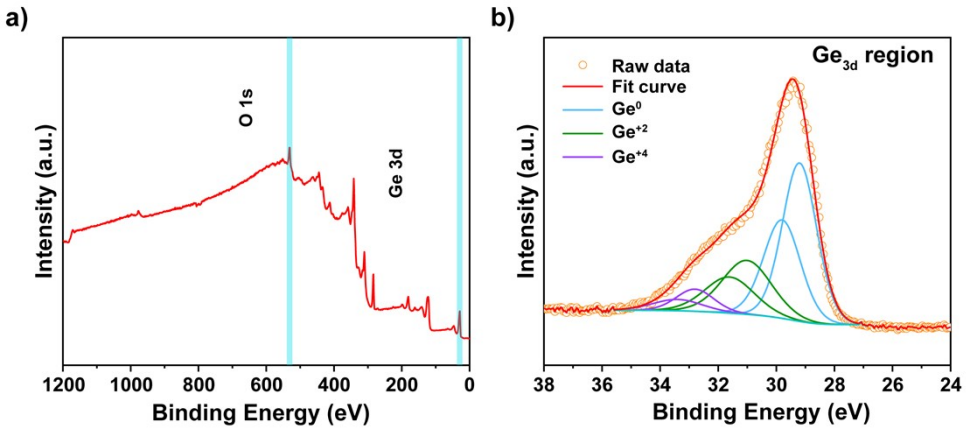

Fig. S1 XPS spectra of Ge NPs: (a) wide scan spectrum and core peaks corresponding to (b) Ge 3d.

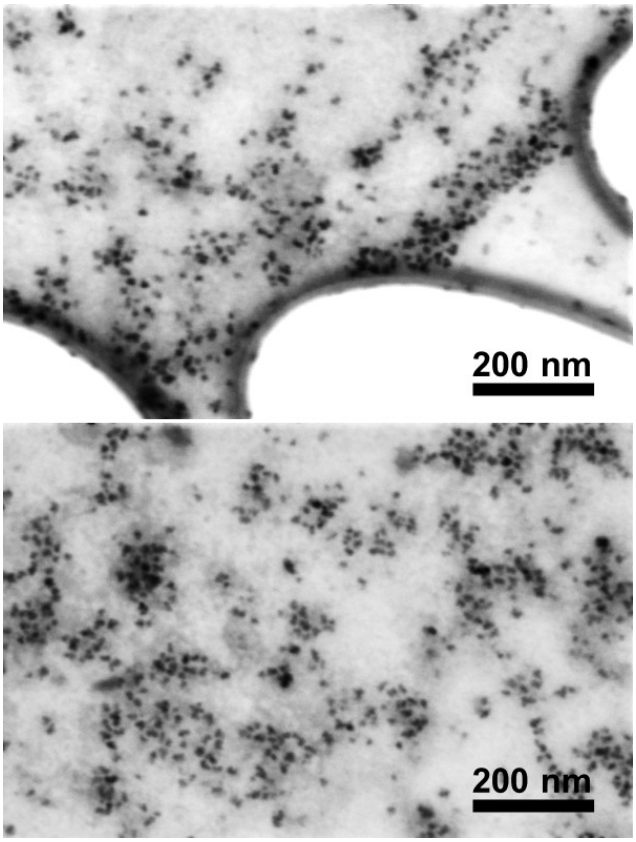

Fig. S2 STEM images (bright mode) of Ge NPs.

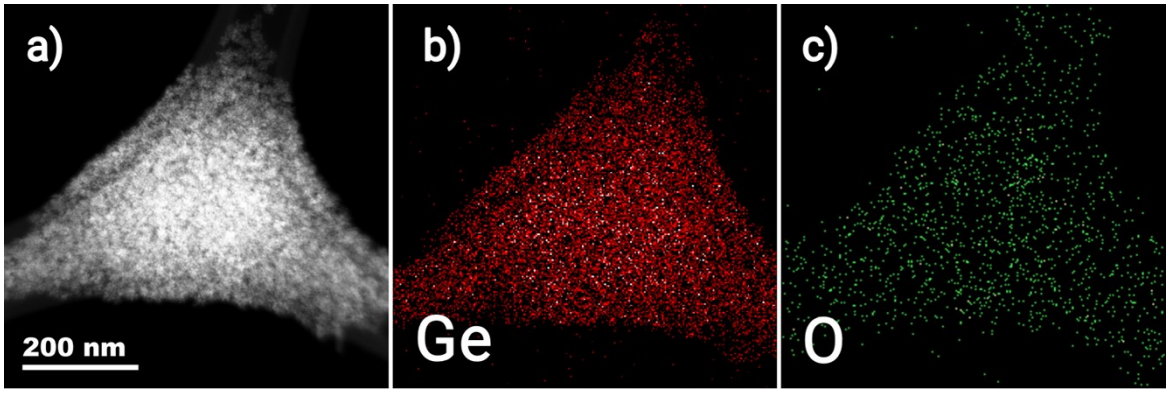

Fig. S3 (a) STEM of Ge NPs and (b, c) EDS mapping of Ge and O elements.

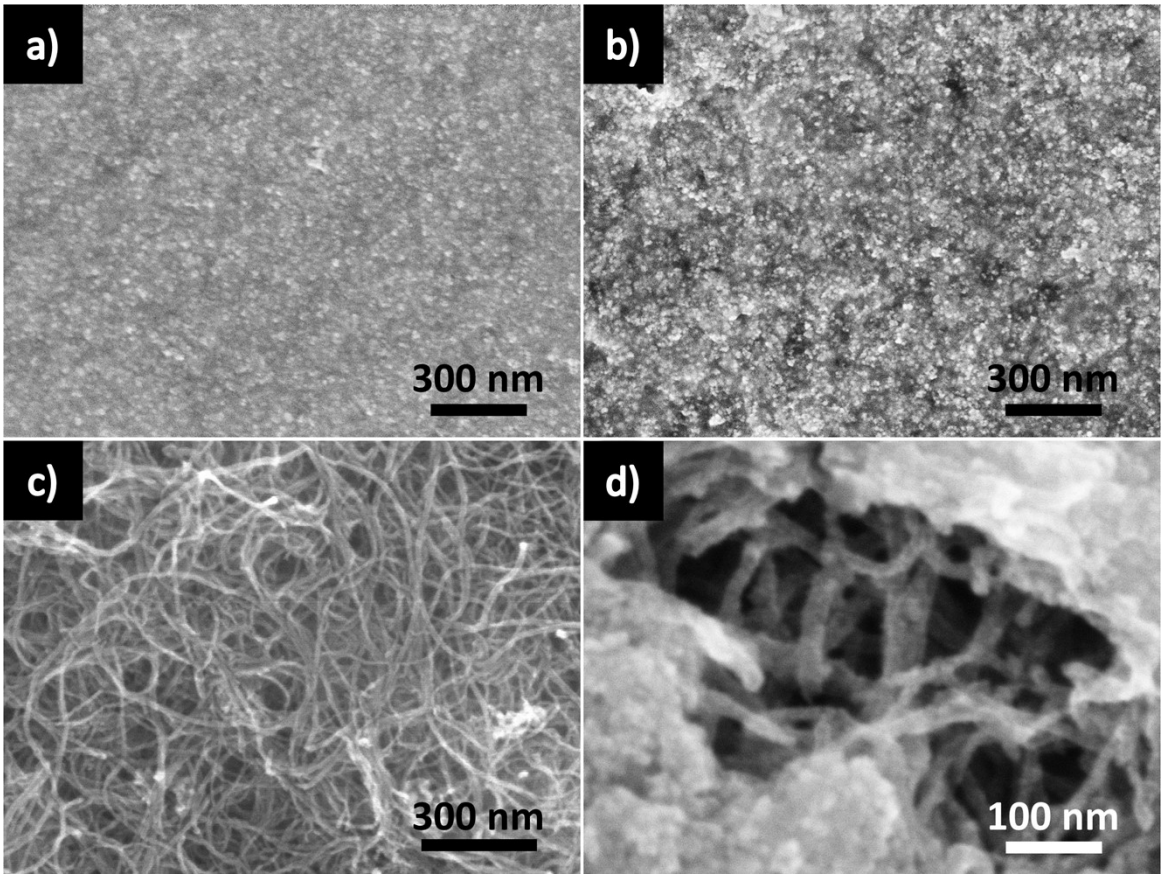

Fig. S4 HR-SEM images of (a) Ge and (b) CNT and (c, d) Ge/CNT deposited by EPD

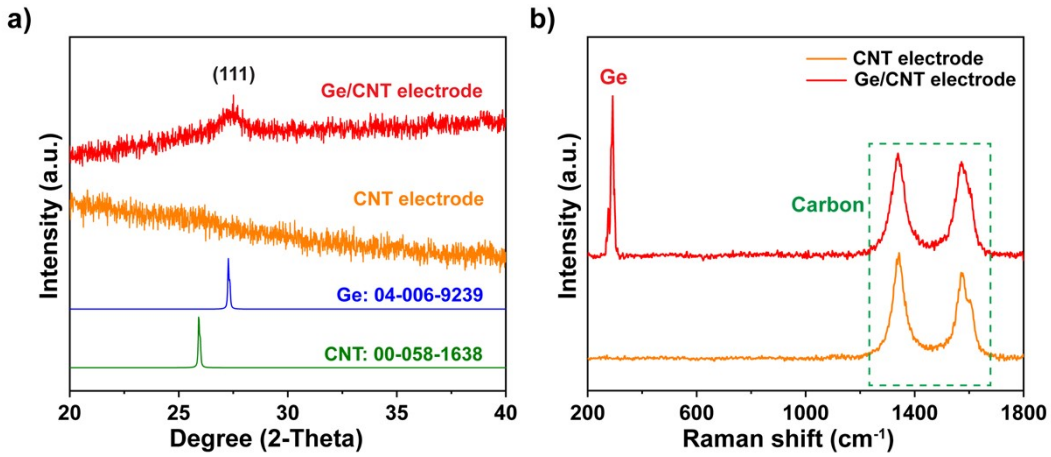

Fig. S5 (a) XRD and (b) Raman spectra of CNT and Ge/CNT electrodes fabricated by EPD.

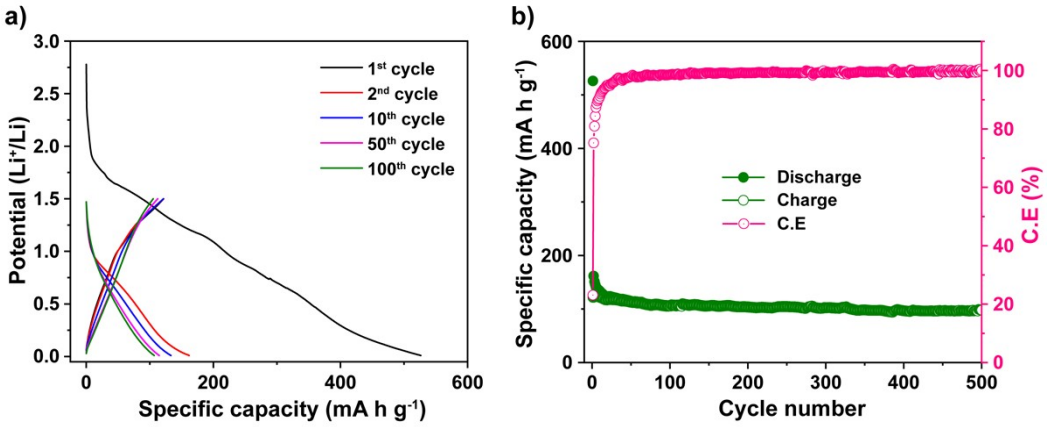

Fig. S6 (a) Discharge-Charge profiles and (b) cycling performance at C/5 of CNT electrode.

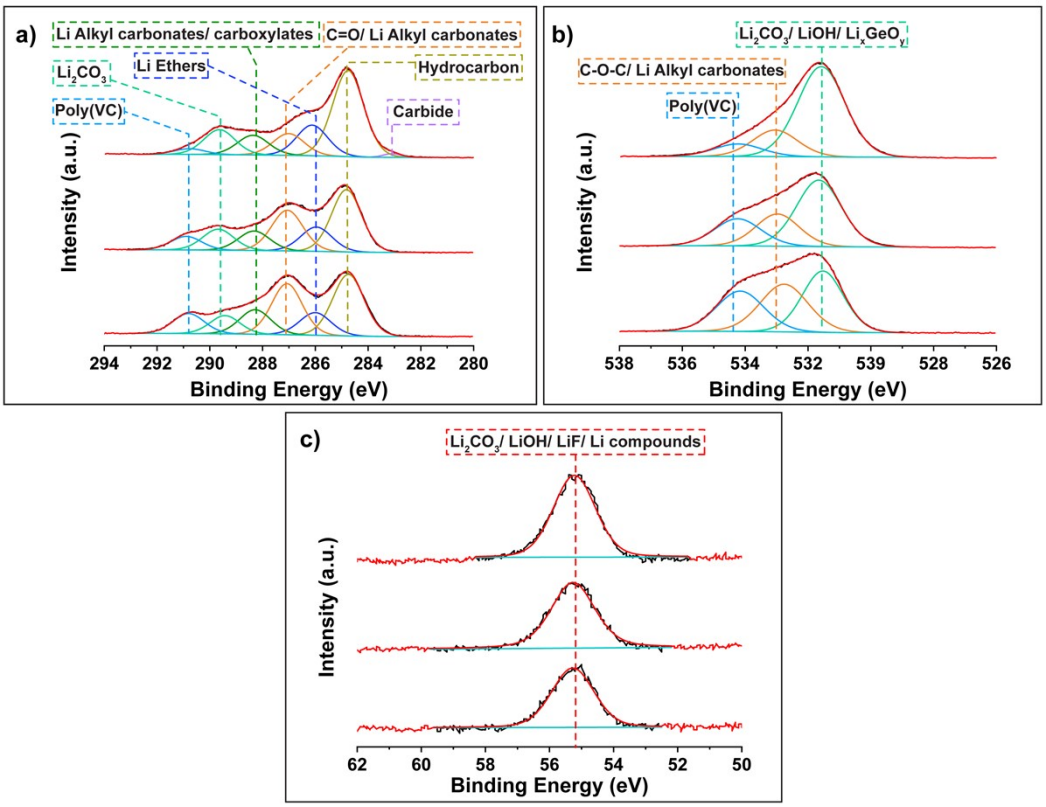

Fig. S7 (a) High-resolution C 1s spectra, b) High-resolution O 1s spectra and c) Li 1s of Ge, Ge/CNT-1 and CNT electrodes after 5 cycles.

The chemical composition of the SEI layer of each electrode after 5 discharge/charge cycles was investigated using XPS analysis. The XPS data revealed that the SEI layer mainly comprises C, O, and Li-containing compounds (Fig. S7). Ge is only found in trace amounts signifying that the thickness of the SEI layer is greater than 10 nm as this is the maximum depth of penetration of XPS. The deconvoluted C_{1s} spectrum (Fig. S7a) shows the composition of SEI layers on all electrodes consists mainly of hydrocarbons, Li ethers, Li alkyl carbonates, Li_2CO_3 and poly(VC) (the electrolyte additive). The most intense peak in each C 1s spectrum occurs at 284.8 eV, assigned to hydrocarbon species in the SEI layer such as alkyl groups.[1, 2] The peaks at 287.1, 288.3, and 288.7 eV correspond to the carbonate species (i.e. Li_2CO_3 and Li alkyl carbonates).[1-4] Other peaks located at 286 and 290.9 eV are associated with Li ethers and polyVC, respectively.[2, 4, 5] One extra peak exists at 283.1 eV in the CNT electrode, corresponding to Li_xC (carbide).[6-8] Analysis of the deconvoluted high-resolution O 1s spectra (Fig. S7b) reveals the presence of a peak for the poly(VC) at 534.2 eV due to the presence of VC which is consistent with the C 1s spectrum. For all electrodes, peaks exist due to the presence of Li_2CO_3/LiOH/Li_xGeO_y (531.6 eV), and the Li alkyl carbonates (533.1 eV).[2, 4, 9] The deconvoluted Li 1s spectrum (Fig. S7c) shows the

existence of LiOH/Li_2CO_3/LiF/Li compounds in the SEI layers of all electrodes.[2, 4, 9] The relative concentrations of each atomic species, corresponding to XPS analysis are shown in Table S1. The relative concentrations of Li 1s (Ge sample) is 13.1%, which is lower than the values of the Ge/CNT-1 (16.1%) and CNT (19.7%) samples. This demonstrates that a considerable amount of Li is consumed in the SEI formation of Ge/CNT-1 and CNT electrodes, resulting in the low CE during a few first cycles.

Table S1 Quantification of each atomic from Survey Spectra

Sample	Atomic %				
	O 1s	C 1s	F 1s	P 2p	Li 1s
Ge	38.2	41.3	5.0	2.4	13.1
Ge/CNT-1	35.9	41.0	5.4	1.6	16.1
CNT	34.7	38.7	5.8	1.1	19.7

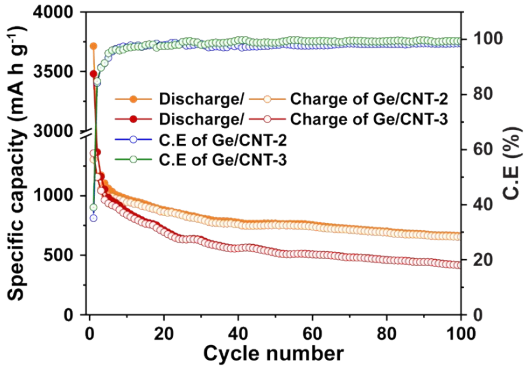

Fig. S8 Cyclability of Ge/CNT-2 and Ge-CNT-3 electrodes.

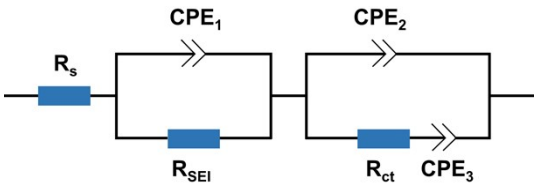

Fig. S9 Equivalent circuit used for fitting of EIS data.

The equivalent circuit includes R_s, R_{SEI}, and Rct which indicate the resistance of the electrolyte, the resistance of the SEI layer and the charge transfer resistance, respectively. CPE_1, CPE_2, and CPE_3 denote the capacitances corresponding to the charge-transfer process.

Table S2 Tabulation of R_s, R_{SEI} and R_{ct} value of Ge/CNT-1 and Ge at different cycle no. cycled.

Electrode	Ge/CNT-1			Ge		
Cycle	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	R_s (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)
1st	9.66	114.7	457	9.88	87.58	1194
10th	7.14	115.8	457.2	6.6	90.08	1251
100th	6.34	143.8	553.4	5.21	145.5	6600

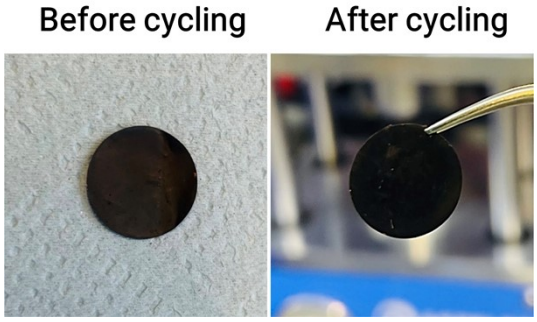

Fig. S10 Optical images of Ge/CNT-1 before and after cycling.

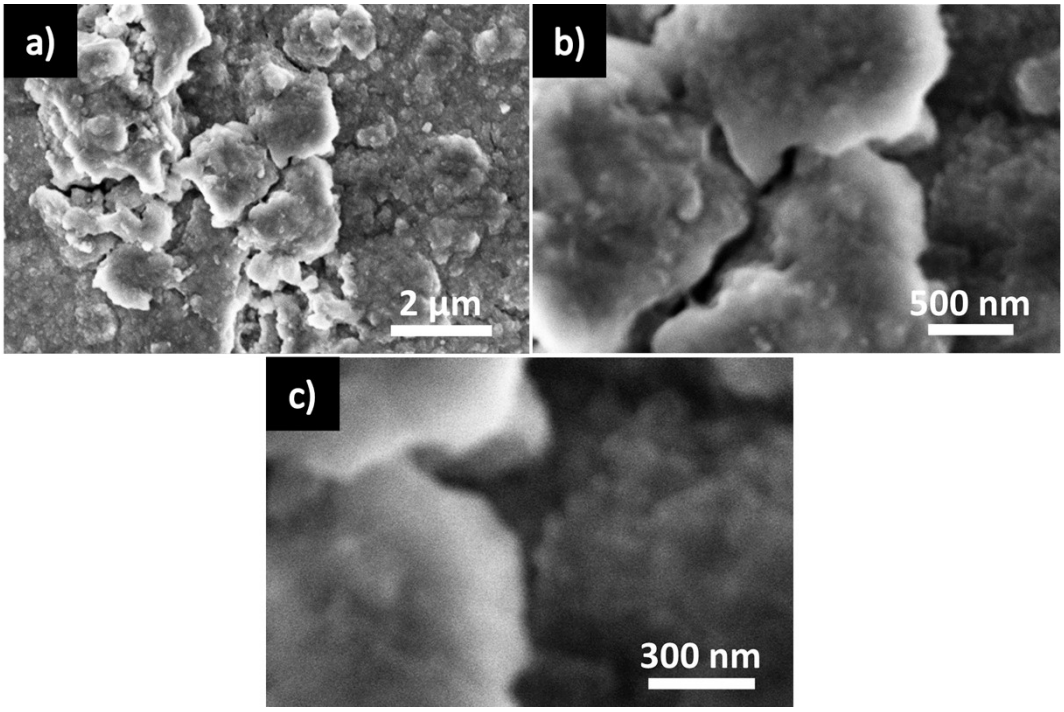

Fig. S11 SEM images (top view) of Ge electrode after 100 cycles.

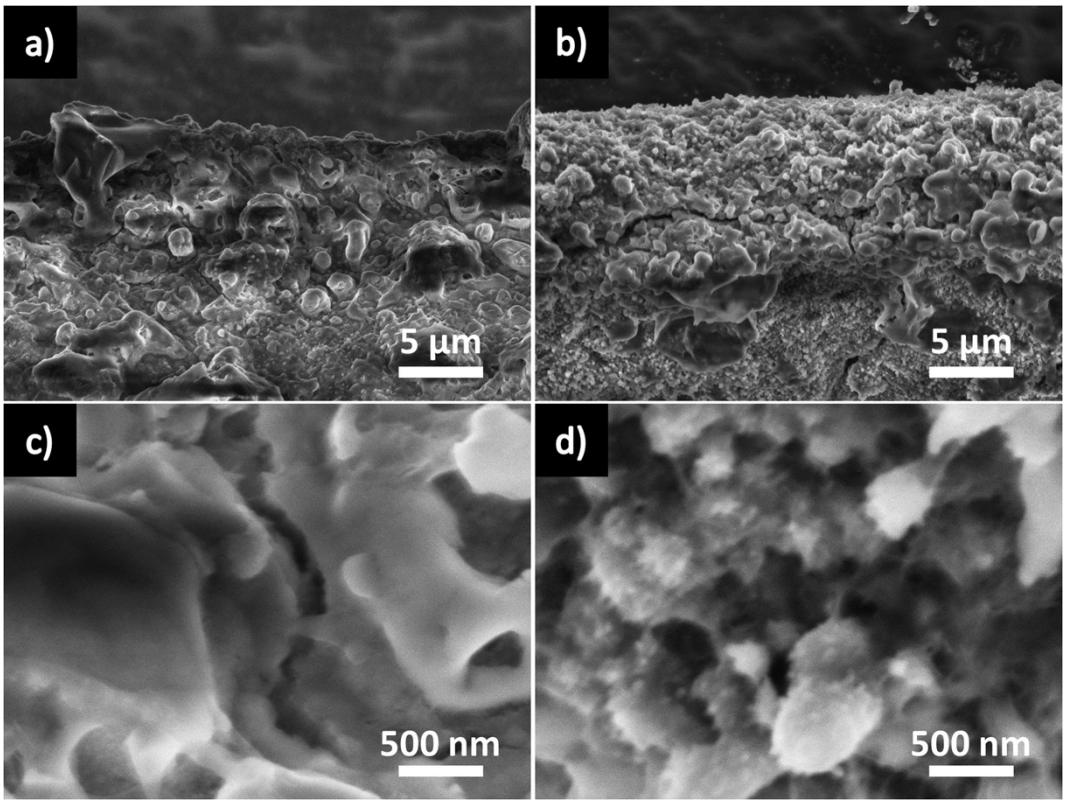

Fig. S12 SEM images (side view) of (a, c) Ge electrode and (b, d) Ge/CNT-1 electrode after 100 cycles.

The side-view SEM images of Ge electrode (Fig. S12a, c) further show the agglomeration of Ge NPs after cycling. In contrast, SEM images of Ge/CNT-1 (Fig. S12b, d) display that the Ge NPs were embedded by the CNT network, accommodating the impact of the volume expansion and agglomeration.

References

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