

Electronic Supplementary Information

**Binder-free Ge Nanoparticles/Carbon Hybrids for Anode Materials of Advanced
Lithium Batteries with High Capacity and Rate Capability**

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Experimental Details

Synthesis of n-butyl capped GeNPs: Anhydrous 1,2-dimethoxyethane was purchased from Aldrich and used without further purification. Inside an Ar-filled glove box, GeCl_4 (1.2g) was dissolved in 1,2-dimethoxyethane (50mL). Sodium naphthalide was used as a reducing agent, which was prepared by through mixing of sodium metal (0.69g; 30mmol) and naphthalene (2.6g; 20mmol) in the presence of 1,2-dimethoxyethane (150mL). After 2h stirring, dark green solution was obtained. The sodium naphthalide solution was injected into the diluted GeCl_4 solution, followed by stirring for 2h. Over the reaction the reduced Ge is formed, as indicated by a clear orange color while the residual reagents are appeared as dark brown precipitates. The orange-colored supernatant was pipette out and transferred to separate round bottom flask. 6 mL of 2.0M *n*-butyllithium was then injected to the orange solution where instant color change from orange to light yellow as well as the formation of white precipitate was seen. The *n*-butyl capped GeNPs were extracted into *n*-hexane and the residual naphthalene was removed by sublimation. This process was repeated until transparent yellow-colored viscous liquid is obtained.

Synthesis of Well-arrayed GeNPs/Carbon Hybrid Anode Active Materials: A poly(styrene-*b*-isoprene) (PS-*b*-PI, 46-*b*-25 kg mol⁻¹, $M_w/M_n=1.04$) is synthesized by sequential high-vacuum anionic polymerization as described in ref [20]. The use of PI chains is expected to help confinement of GeNPs within nanoscale morphology of PS-*b*-PI on account of the similar solubility parameter of isoprene to that of butyl-capped surface of the GeNPs. Pre-weighed amounts of the butyl-capped GeNPs and the PS-*b*-PI are dissolved in the mixture of toluene and *n*-hexane (70:30 vol.%). Thermoset polymer was prepared by mixing 0.4g of phenol, 2, 4, 6-tris(dimethylamino methyl), 4.4g of nadic methyl anhydride, 5.4g of dodecenylsuccinic anhydride, and 10.2g of Poly/Bed[®] 812, which were purchased from polyscience. The GeNPs containing PS-PI in toluene/*n*-hexane and the thermoset polymer were then mixed with 70:30 weight ratio with an aid of THF. Under vigorous stirring, the solution was pre-cured at 65

°C for 1h, followed by drop coating onto the mirror-polished stainless steel substrate (SS). The resulting film was exposed to additional curing at 65 °C for 3h and then pyrolysed at 800 °C under Ar/H₂ flow for 1h. Fixed heating rate of 20 °C/min was used.

Synthesis of Polymer Electrolytes: A poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO, 22-*b*-35 kg mol⁻¹, M_w/M_n=1.08) is synthesized by sequential high-vacuum anionic polymerization as described in ref [20]. PS-PEO is then blended with PEO homopolymer (3.4 kg/mol, purchased from Aldrich) with a weight ratio of 80:20 where the PEO phase is doped with LiClO₄ salts at a fixed concentration of [Li⁺]/[EO]=0.056 using 50/50 vol.% THF and methanol mixture. Solutions were stirred overnight at room temperature and the dried samples were pressed into 200 μm thick disks using a mechanical press with pressures of up to 2000 psi at 80°C. Through-plane conductivity of prepared solid polymer electrolytes was measured using a homemade test cell on thermostated pressed samples, using a Solartron 1260 frequency response analyzer connected to a Solartron 1296 dielectric interface. All procedures were performed inside the glove box with oxygen and moisture level of 0.1 ppm.

Morphology Characterization: The butyl-capped GeNPs/PS-PI/thermoset polymer hybrid after thermal curing (before pyrolysis) was cryo-microtomed at -120 °C to obtain thin sections with thicknesses in the 80 – 120 nm range using using an RMC Boeckeler PT XL Ultramicrotome. The electron contrast in the samples was enhanced by exposure to osmium tetroxide (OsO₄) vapor for 50 min. After pyrolysis, the cross-sectional anode materials comprising GeNPs/carbon/SS was prepared with a FEI Strata 235 Dual Beam focused-ion beam (FIB) using 30 keV Ga⁺ beam. Ru protection layers of air surface are aimed to minimized beam damage during milling process. Samples were characterized with a JEOL JEM-2100F microscope operated at 200 kV. X-ray diffraction analysis on anode materials was carried out at the POSTECH (Rigaku D/MAX-2500, CuKα, λ=1.54Å). Synchrotron SAXS measurements on the solid polymer electrolytes were performed using the 10C SAXS beam line at Photon Factory, Japan.

Battery Cycle Tests Using Coin-type Half Cells: The binder-free GeNPs/carbon hybrid anode active materials prepared by pyrolysis are used for the battery testing. The home-built coin-type half cell consists of the GeNPs/carbon hybrid anode materials, solid polymer electrolyte, and Li foil. No separator was used. Different C rates from 1C to 10C (1C=1600mA g⁻¹) were used for cycling tests in which the charge and discharge rates were identical. The battery cycle temperature was fixed at 65 °C.

20 N. Hadjichristidis, H. Iatrou, S. Pispas, M. J. Pitsikalis, *Polym. Sci., Part A: Polym. Chem.* 2000, **38**, 3211.

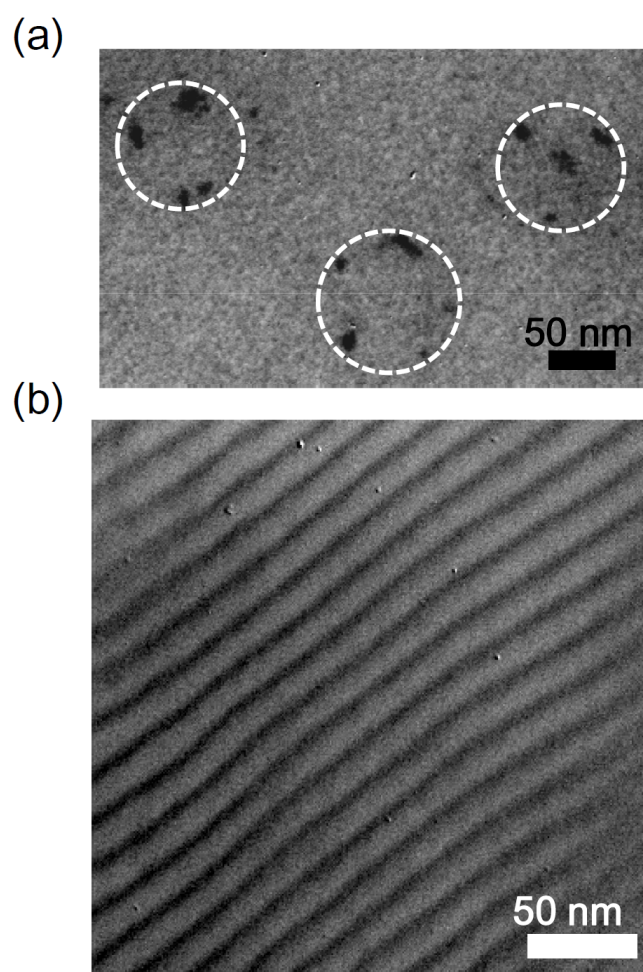


Figure S1. TEM images of (a) thermally cured GeNPs/PS-PI/thermoset polymer composites obtained without staining and (b) cryo-microtomed PS-PI confirming lamellar morphology. The dotted circles in (a) indicate the expected sizes of PS-PI particles, embedded in the thermoset polymer matrix.

The GeNPs/carbon hybrid revealed porous characteristics although, the TEM images in Figure 1b were taken from nonporous area. In present study, all TEM samples of anodes were prepared by FIB-TEM and we found that the ion-milling and lift-out were problematic for porous regions since the processes enlarge the pores. Instead, SEM was utilized to take surface topology of the GeNPs/carbon hybrid anode. SEM images of the GeNPs/carbon hybrid anode are shown below to demonstrate the porous structure with pore sizes ranging from 20 to 200 nm.

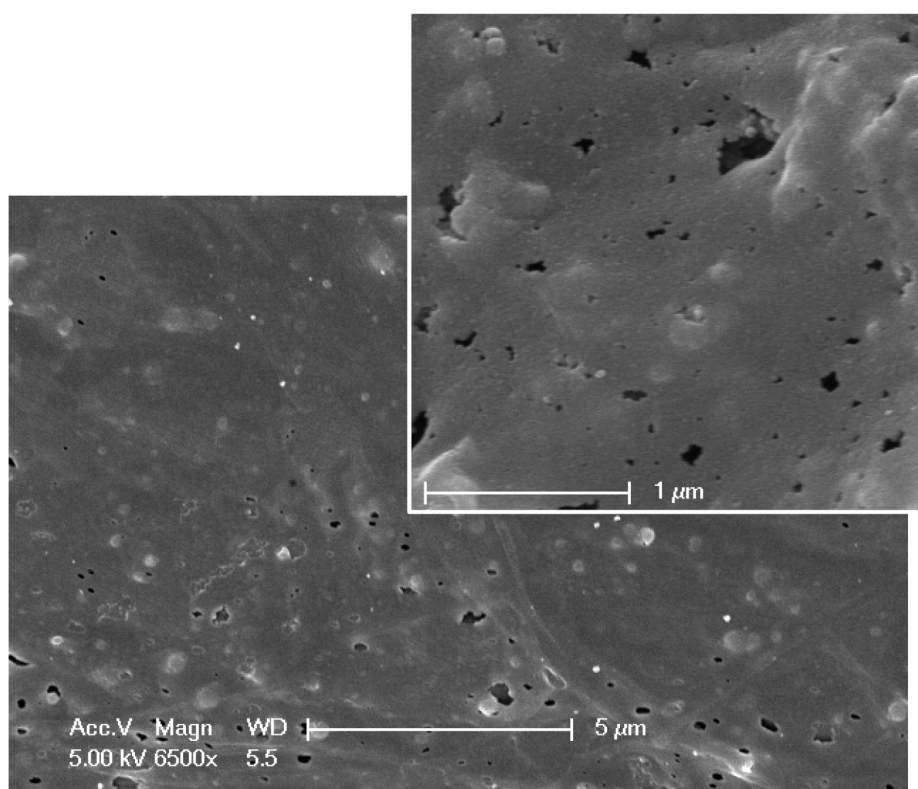


Figure S2. SEM images of the pyrolysed GeNPs/carbon hybrid anode.

The PS-PEO (22K-35K)/PEO (3.4K) exhibits lamellar morphology with domain spacing of 26 nm before salts doping. After doping with LiClO₄ salts at a fixed concentration of [Li⁺]/[EO]=0.056, the domain spacing increases to 31 nm with improved degree of ordering due to the increased segregation strength between hydrophobic PS blocks and hydrophilic PEO blocks. From the temperature-dependent conductivity data of LiClO₄ doped PS-PEO/PEO, the battery cycle temperature was fixed at 65 °C where the ionic conductivity of the solid electrolyte is 4×10⁻⁴ S/cm.

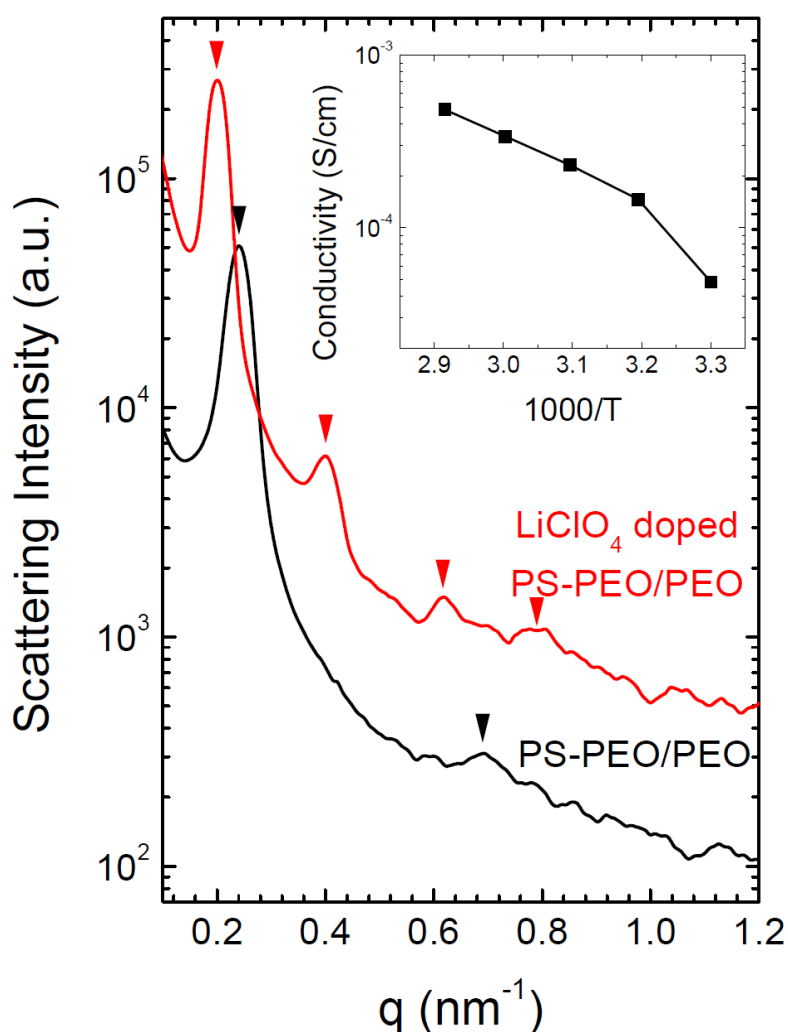


Figure S3. SAXS profiles of PS-PEO (22-35 kg/mol)/PEO (3.4 kg/mol) before and after LiClO₄ doping. The scattering profiles are vertically offset for clarity. The inverted filled triangles represent Bragg peaks at q*, 2q*, 3q*, and 4q* indicative of lamellar morphology. Temperature-dependent conductivity data of LiClO₄ doped PS-PEO/PEO are shown in the inset plot.

Charge/discharge capacities of carbon sheathed GeNPs at different C rates are given in the figure below as a function of cycle number. The results demonstrate poor rate capacities of carbon sheathed GeNPs at high C rates as well as low capacity retention (only 32% of the initial capacity) when the cycle rate was returned back to 1C.

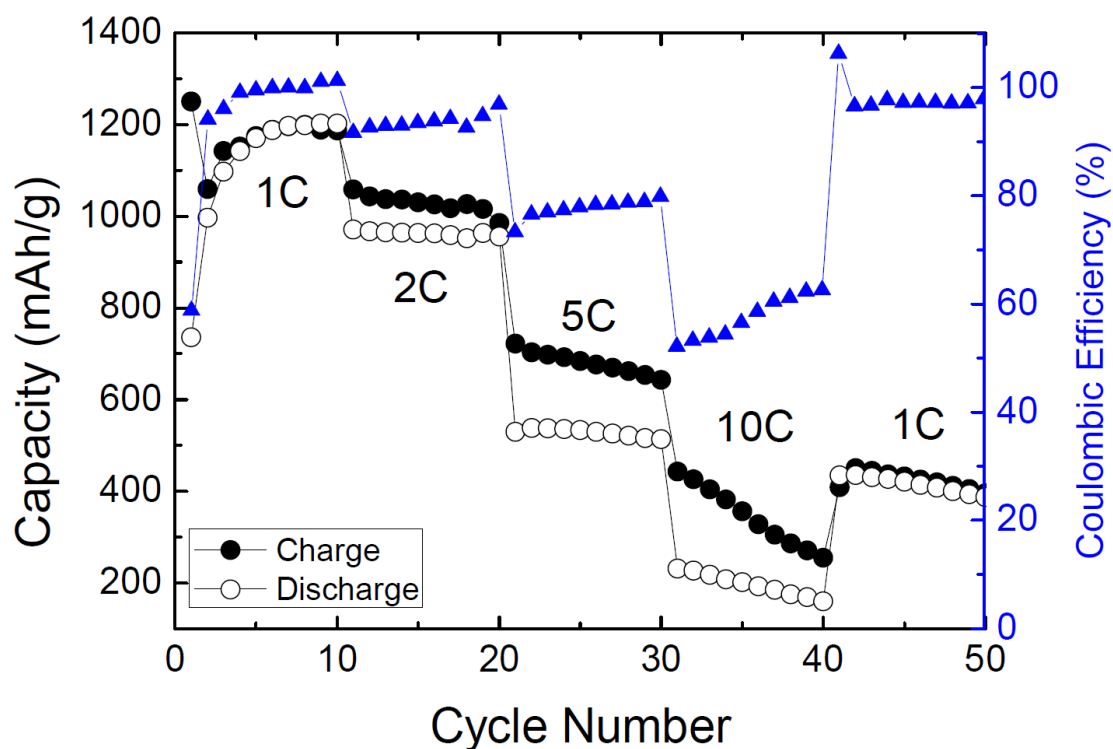
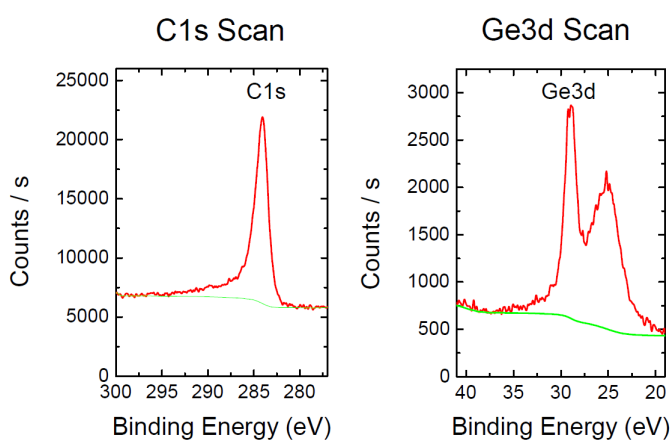


Figure S4. Charge/discharge capacities of carbon sheathed GeNPs at different C rates vs. cycle number. Coulombic efficiency of the carbon sheathed GeNPs is plotted on the right axis.

We carried out X-ray photoelectron spectroscopy (XPS) to characterize atomic compositions of the anodes. The Ge:C weight ratios were calculated as 52:48 and 64:36 for GeNPs/carbon hybrid and carbon sheathed GeNPs, respectively. As expected, the carbon amount in GeNPs/carbon hybrid is greater than that in carbon sheathed GeNPs, however, it is not marked different. This implies that the carbon content in the anode shouldn't play a central role on the improved battery performance of the GeNPs/carbon hybrid. XPS spectra of both electrodes are given below.

(a) GeNPs/carbon hybrid



(b) Carbon sheathed GeNPs

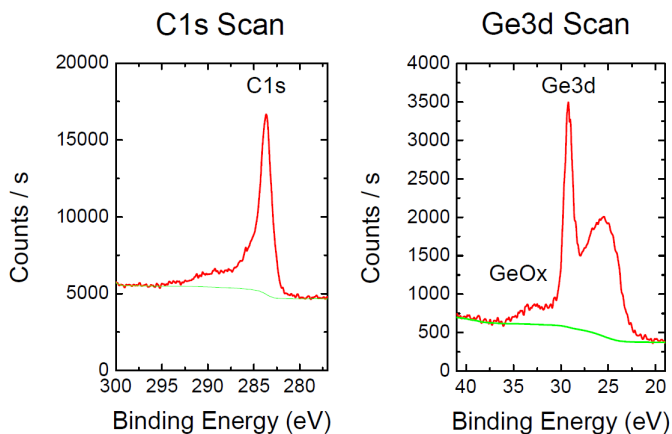


Figure S5. XPS results of (a) GeNPs/carbon hybrid and (b) carbon sheathed GeNPs.

From ex-situ FIB-TEM experiments of cycled anodes, we confirm that the internal morphology of the GeNPs/carbon hybrid is not hurt by the repeated lithiation/de-lithiation although the crystalline Ge becomes amorphous. The fact that the same 10nm-sized GeNPs were seen after 50 cycles clearly demonstrates the role of 3-dimensional arrangement of GeNPs in carbon matrices to maintain the particle size and shape during cycling. In contrast, the aggregation and pulverization of non-organized GeNPs were evident, which should attribute to the capacity fade upon impeding the electrons and Li^+ transport.

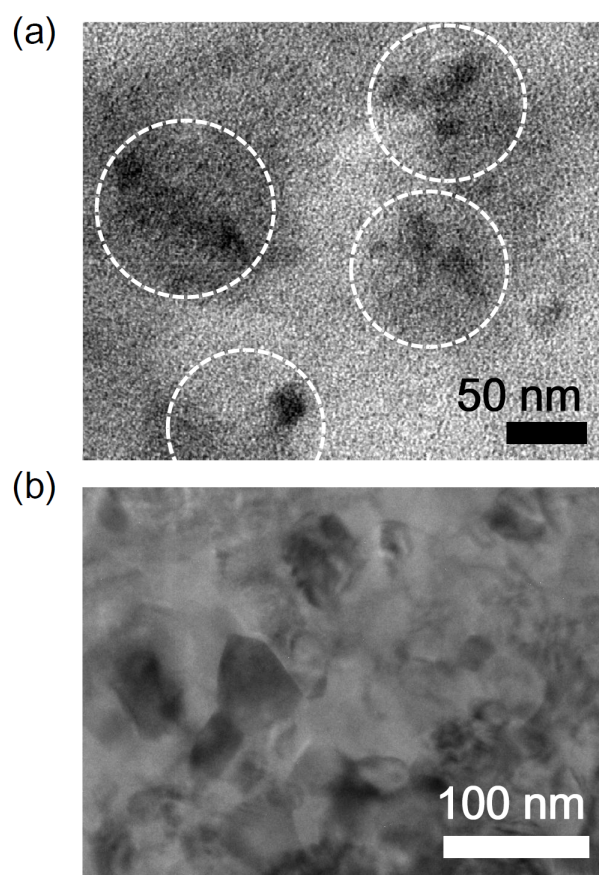


Figure S6. *Ex-situ* FIB-TEM images of the cycled anodes after 50 cycles; (a) GeNPs/carbon hybrid and (b) carbon-sheathed GeNPs anode lacking organization.

We compared Nyquist plots of GeNPs/carbon hybrids and carbon sheathed GeNPs before and after charge/discharge cycles. Before charge/discharge cycles, two electrodes indicate qualitatively similar impedance profiles. After charge/discharge cycles, however, the impedance profile of the carbon sheathed GeNPs anode contrasted sharply with that of the GeNPs/carbon hybrid anode. A large increase in electrolyte/electrode resistance was observed for carbon sheathed GeNPs anode as a result of battery cycling, which should be attributed to the pulverization/aggregation of GeNPs during repeated lithiation/de-lithiation cycles.

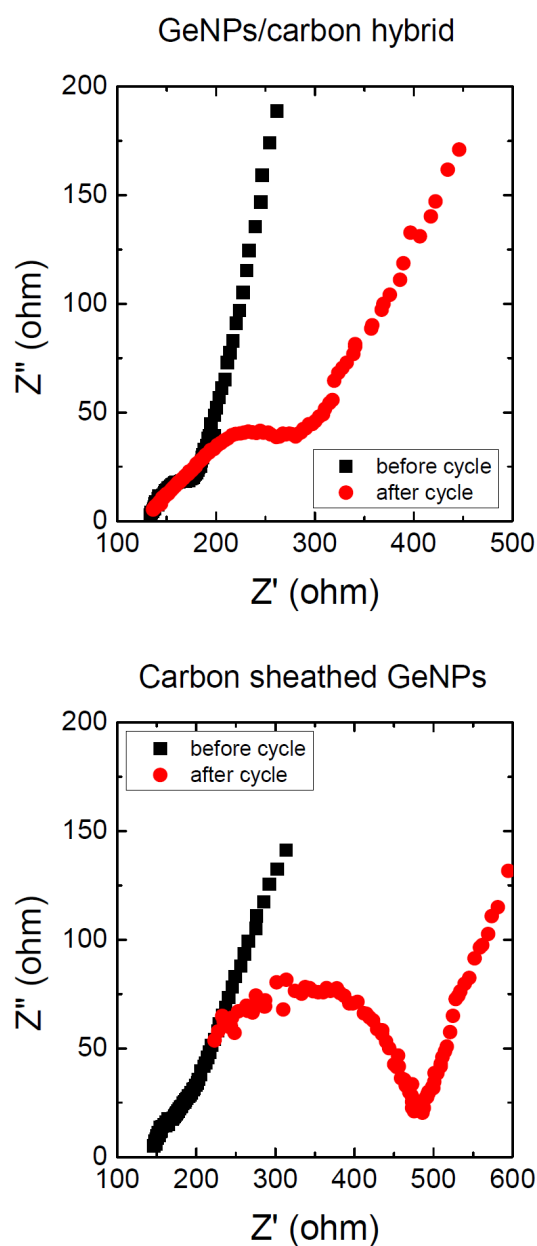


Figure S7. Nyquist plots of GeNPs/carbon hybrids and carbon sheathed GeNPs before and after charge/discharge cycles.