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Supplementary Information for

Binder-free Ge-nanoparticle anode assembled on multiwalled carbon nanotube networks for Li-ion batteries

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Experimental procedures

Pristine MWCNTs (2 g, CM 100, Hanwha Nanotech) were added to a 3:1 mixture of H_2SO_4 and HNO_3 (98%, 70%, Samchun Chem.) to form carboxylic functional groups on the MWCNT surfaces. Then, the mixture was heated with vigorous stirring and allowed to stand at 110 °C for 30 min. After the acid treatment, the MWCNTs were washed with deionized water and absolute ethanol, and filtered through a polyvinylidene fluoride (PVDF) membrane (Durapore, 0.22 mm Millipore); the washing and filtering were performed several times for the purification of acidic residues. The washed MWCNTs were first dried in a N_2 stream at room temperature, and then dried for 8 h in a vacuum oven at 80 °C. For the formation of an MWCNT film on a substrate, 20 mg of functionalized MWCNTs and 4 mg of $Ni(NO_3)_2 \cdot 5H_2O$ (Samchun Chem.) were added to 50 mL of isopropyl alcohol and dispersed by using a bath-type ultrasonicator for several hours. Afterward, cathodic electrophoretic deposition of the well-dispersed MWCNT suspension was performed under a constant voltage of 100 V for 2 min with a 304 SS foil (0.03-mm thickness, Alfa Aesar) negative electrode (cathode) and an Al foil anode, which were supported by slide glasses. The electrophoretically deposited MWCNT films were dried at 80 °C by keeping them in a vacuum oven for 4 h.

The Ge (99.80%, 325 mesh, Alfa Aesar) source and pre-deposited MWCNT substrates were located in the two different temperature regions. An alumina boat filled with 0.4 g of Ge source was placed in the middle of the hot zone, and the circle-type EPD MWCNTs on the SS were located near the cold zone of the furnace. Before evaporation, an enclosed quartz tube was evacuated to 10^{-3} Torr using a rotary pump. Ar was introduced into the quartz tube at a constant flow rate of 100 sccm to maintain the pressure of the reactor within the range 2.0–3.0 Torr. The hot and cold zones of the furnace were heated to 700 °C and 480 °C, respectively. After evaporation for 30 min, the furnace cooled down to room temperature. Finally, Ge-nanoparticle-deposited MWCNTs were obtained on the SS substrate.

The properties and structural morphologies of the prepared films were characterized by X-ray diffraction (XRD, D/max-2500V/PC, Rigaku), field-emission scanning electron microscopy (FESEM, JSM-6330F, JEOL), transmission electron microscopy (TEM, JEM-2100, JEOL), and energy-dispersive X-ray spectroscopy (EDX).

The weight of the deposited film was measured by a microbalance (0.1 μg, model UMT5, Mettler Toledo, Greifensee, Swiss). The electrochemical performances of the prepared films were evaluated using Swagelok-type half-cells. The Ge-MWCNT composite fabricated on the SS substrate was punched with a diameter of 10 mm for the direct test. The half-cells were assembled using a punched Ge-MWCNT electrode as the positive electrode (cathode), a Li metal foil as the negative electrode (anode), a separator film (Celgard 2400), and a liquid electrolyte (ethylene carbonate and dimethyl carbonate (1:1 by volume) with 1.0 M LiPF6, Techno Semichem Co., Ltd., Seongnam, South Korea). The assembled cells were cycled galvanostatically between 2.5 and 0.01 V using an automatic battery cycler (WBCS 3000, WonaTech, Seoul, Korea), and cyclic voltammetry was carried out at a scan rate of 0.3 mV s^{-1}. Each cell was cycled over the voltage window 0.0–1.2 V versus Li/Li^+ at a rate of 1 C (=1624.55 mA g^{-1}) for 200 cycles. Various discharge/charge current densities (0.5 C, 1 C, 2 C, 3 C, and 5 C) were imposed on the Ge EPD MWCNT electrode over the voltage range 0.0–1.2 V for investigation of the rate capabilities.

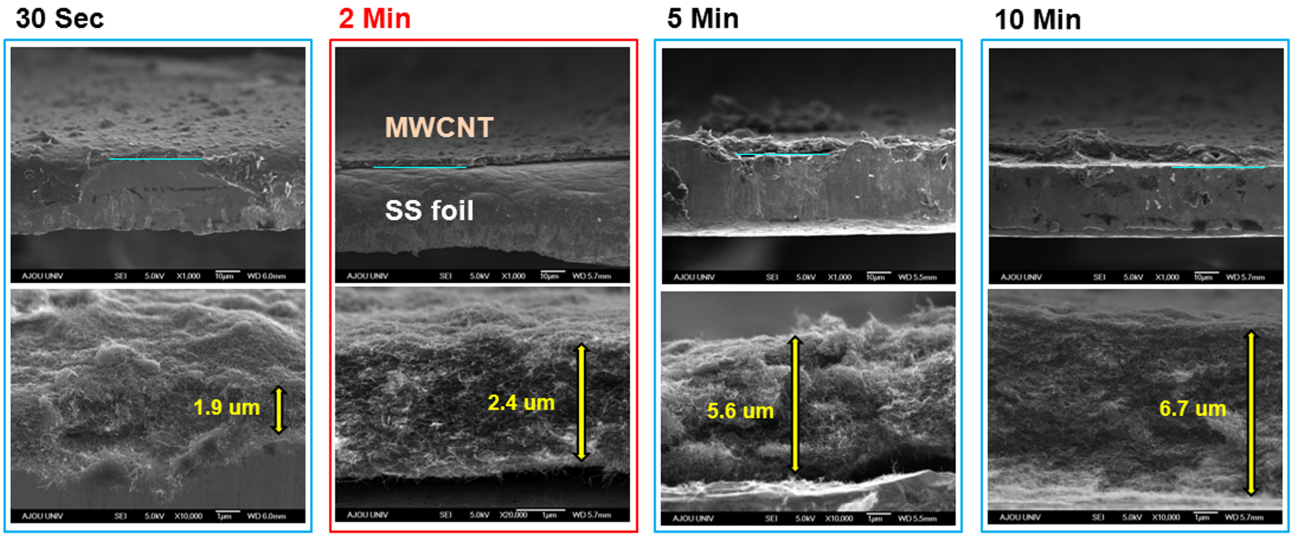

Fig. S1. Cross-sectional SEM images of the MWCNT film obtained by electrophoretic deposition on a SS substrate as a function of deposition time.

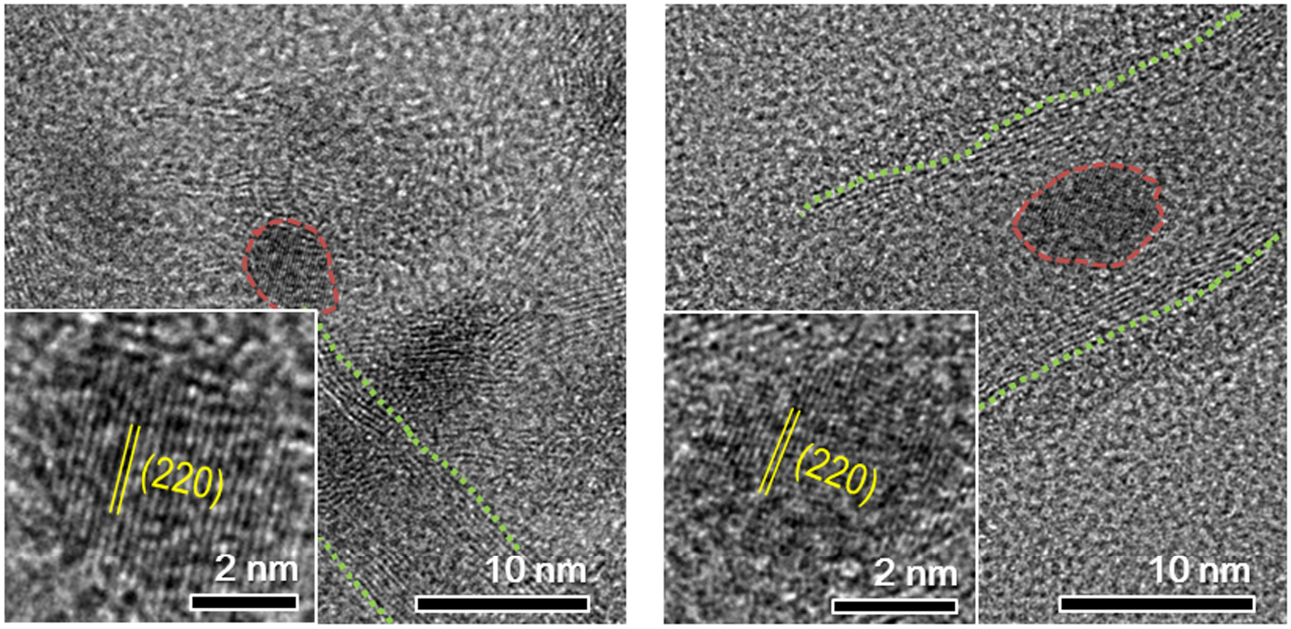

Fig. S2. Typical HRTEM images of Ge-MWCNT nanocomposites.

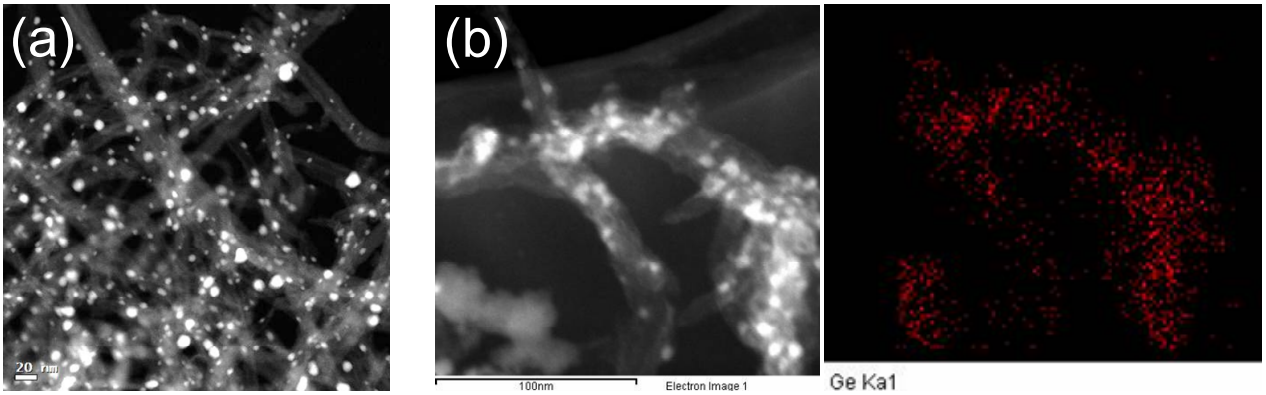

Fig. S3. (a) HAADF image and (b) EDS elemental mapping result of Ge-MWCNT nanocomposites prepared after evaporation for 60 min, showing the uniform distribution of Ge nanoparticles.