Confined metal Ge quantum dots in carbon nanofibers for stable rechargeable batteries

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Experimental

Materials synthesis

In a typical synthesis procedure, polyacrylonitrile (0.6 g, PAN, MW150000, Aldrich) were dissolved in N, N-dimethylformamide (5 mL, DMF, Aladdin), and then germanium isopropyl solution (1 mL, Alfa Aesar) were added. Next, the mixed solution was dispersed by stirring for 3 h. The precursor solution was introduced into a plastic syringe connected to a stainless steel needle with an internal diameter of 0.9 mm. The flow rate was set at 0.2 mL min^{-1} by using a precision propeller and an aluminium foil was placed at a distance of 15 cm to collect the nanofibers. A voltage of 15 kV was applied by a high voltage power supplier. The above procedure requires fine weather with humidity below 50%. The as-prepared nanofiber membrane precursor with an area of ~ 100 cm^2 was first dried in an electric vacuum oven (100 ˚C, 12 h) and then annealed in a tube furnace (700 ˚C, 8 h) with a heating rate of 10 ˚C min^{-1} (atmosphere: Ar + H_2, 95 : 5 by volume). The final Ge/CNFs product exhibits black membrane appearance. CNFs were prepared in the same procedure with the absence of germanium isopropyl. Pure Ge was purchased from Aladdin reagent company (> 200 mesh).

Characterizations

To analysis the morphologies and microstructures of the samples, scanning electron microscopy (SEM, Hitachi S-4800), transitions electron microscopy (TEM, JEOL JEM-2100F), high resolution TEM (HRTEM) accompany with selected area electron diffraction (SAED) were employed. TEM energy dispersive spectrum (EDS) was used to obtain the elemental maps of Ge/CNF. The surface elements were analyzed using an X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD); powder X-ray diffraction analysis (XRD, Philips, PW 1830) was carried out to evaluate the phase structures of the samples between 10˚ and 90˚ at a scan rate of 6˚ min^{-1}. The surface area was determined by nitrogen adsorption/desorption using the Brunauer–Emmett–Teller method (BET, Nova2200e). Raman spectrum was recorded by a RM-1000 Renishaw confocal Raman micro-spectroscope with 514.5 nm laser radiation at a laser power of 0.48 mW in the range of 200 ~ 2000 cm^{-1}. TGA was performed using a Pyris Diamond TG/DTA (PerkinElemer Inc., USA). Samples were heated from room temperature to 800 ˚C at the heating rate of 10 ˚C min^{-1} in air.

Electrochemical measurements

Both of Ge/CNFs and CNFs membranes were cut into disks with a diameter of 14 mm (~ 5 mg) and directly used as electrodes without binder and conductive reagents (see ESI, Fig. S1). Pure Ge electrodes were fabricated by using the same procedure as reported in our previous work.[1] 2032 type coin cells were assembled in an Ar-filled glove box with lithium metal foil as counter electrode, polypropylene (PP) micro-porous film as separator and 1 M $LiPF_6$ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1 : 1 by volume) as the electrolyte. Cyclic voltammetric (CV) tests were performed on an electrochemical workstation (Zennium, IM6, Germany) at a scan rate of 0.2 mV s^{-1} between 0.0 and 3.0 V. The galvanostatic charge/discharge cycling tests were carried out between 0 and 1.5 V at different current densities on a LAND BT2013A battery tester. Electrochemical impedance spectroscopy (EIS) technique was performed to measure impedance in the frequency range from 0.01 Hz to 100 kHz by using the same type electrochemical workstation as above.

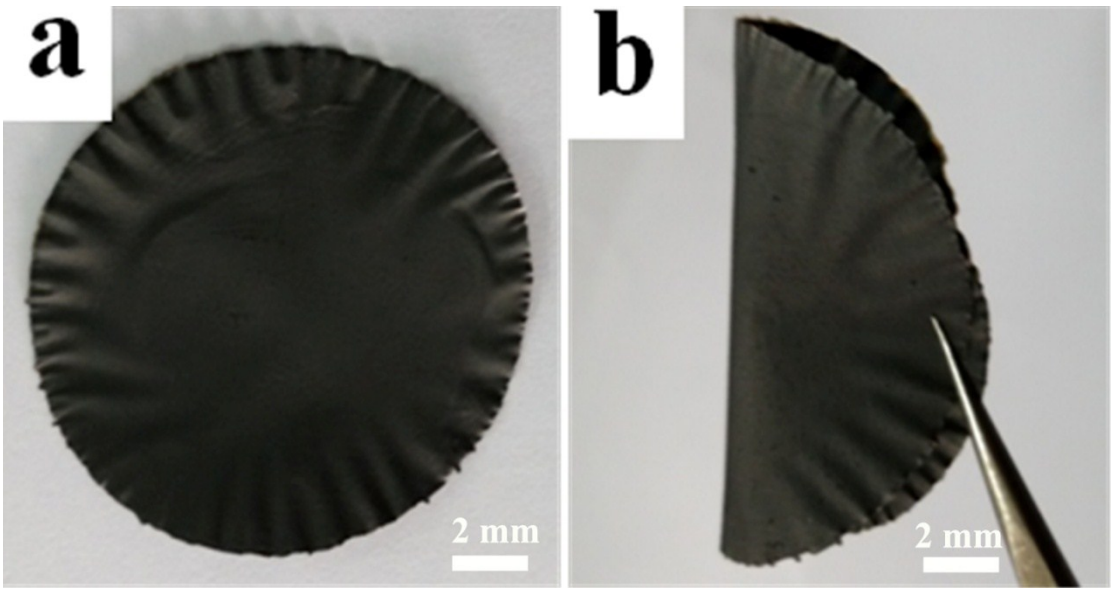

Figure S1. Ge/CNFs electrodes were directly cut from the Ge/CNFs membranes.

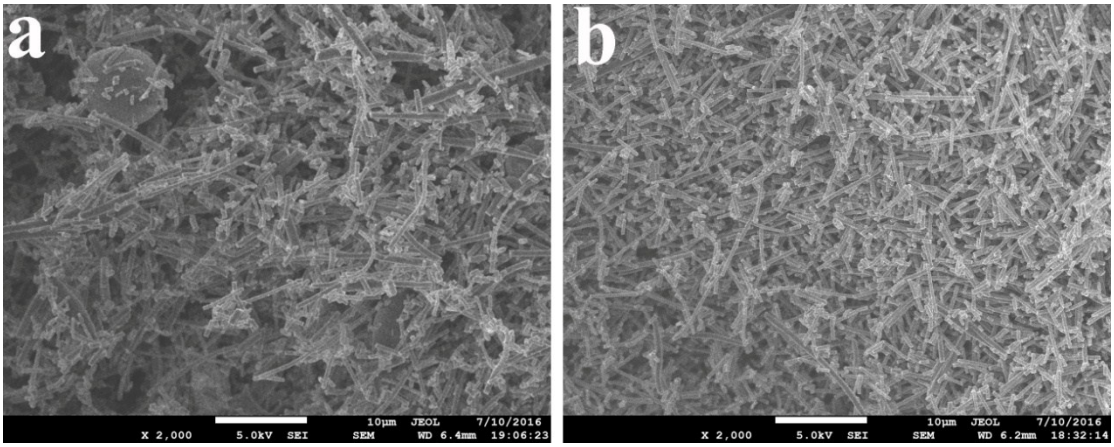

Figure S2. SEM images of (a) Ge/CNFs and (b) CNFs electrodes after 100 cycles. From the SEM images it is clear that most of the Ge/CNFs can maintain their original 1D structure.

References

1. W. Wei, F. Jia, P. Qu, Z. Huang, H. Wang, L. Guo, *Nanoscale*, 2017, **9**, 3961