Electronic Supplementary Material (ESI) for Energy & Environmental Science
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Supporting Information

A New Catalyst-embedded Hierarchical Air Electrode for High-performance Li−O_2 Batteries

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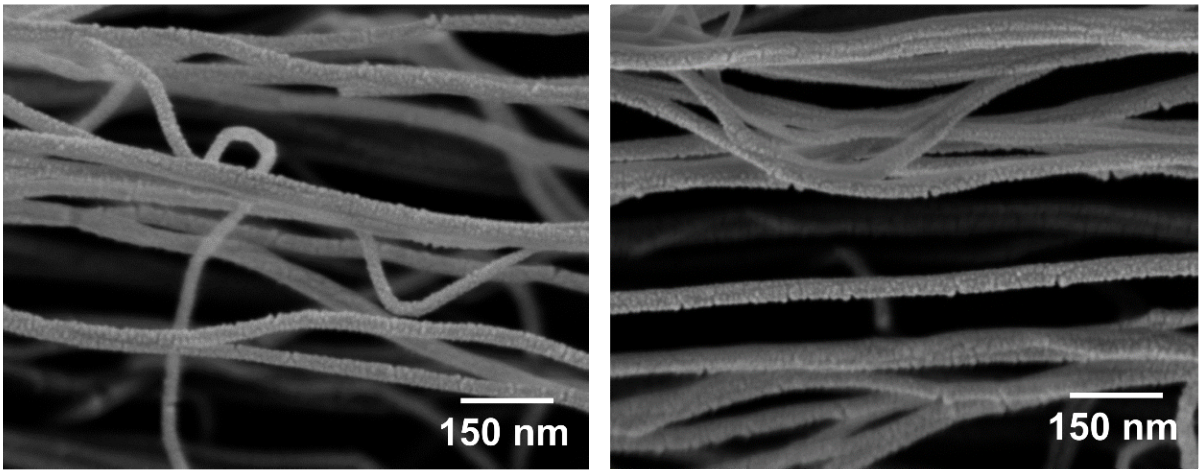

Figure S1. SEM images of the Pt/CNT electrode. The scabrous surface texture indicates that all of the individual CNT strings are homogenously coated with Pt nanoparticles.

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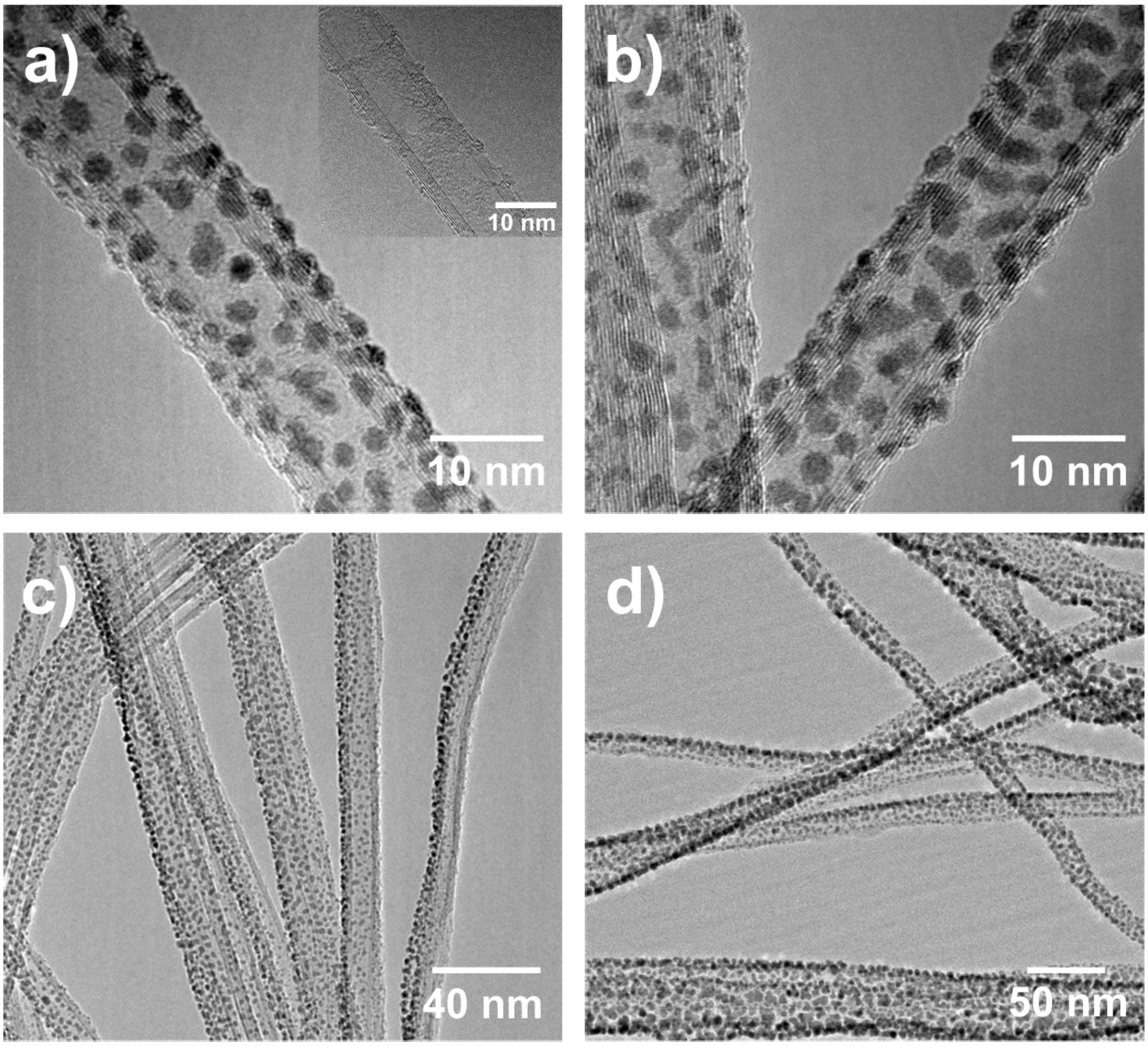
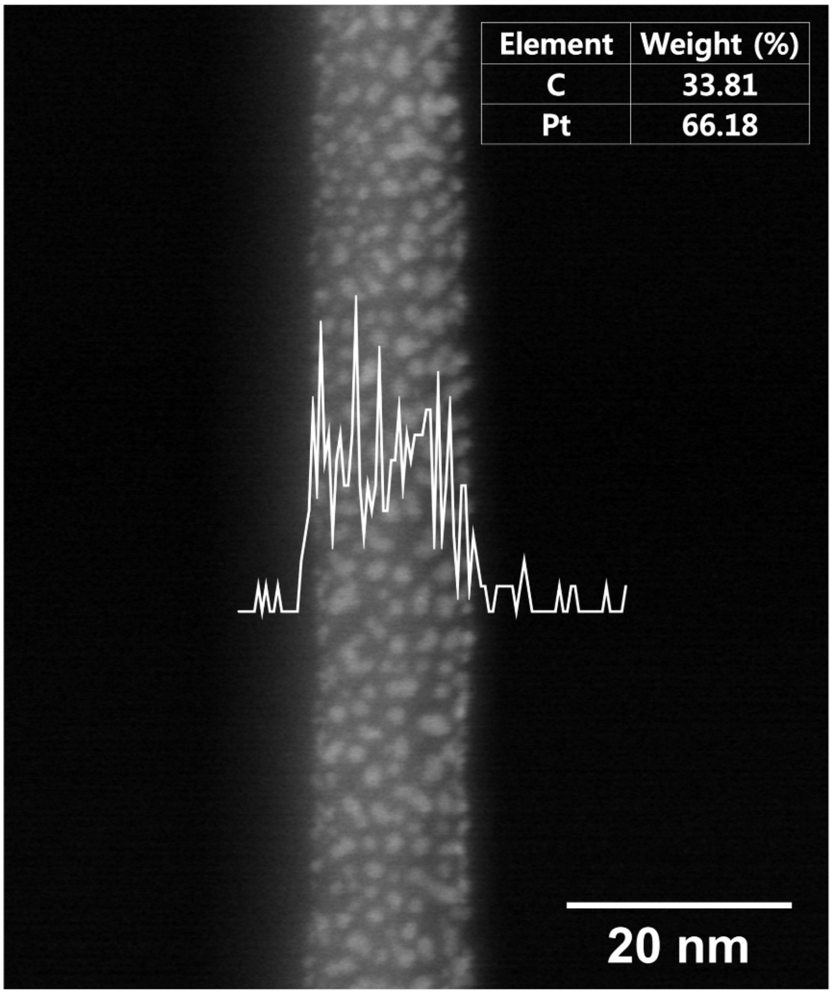


Figure S2. Additional TEM images of the Pt/CNT electrode at various magnifications (Inset: TEM image of the as-prepared CNT).



Element	Weight (%)
C	33.81
Pt	66.18

Figure S3. TEM image of a single string of Pt/CNT at a high magnification and the EDS line map of Pt. The inset table shows the quantitative analysis of Pt and C.

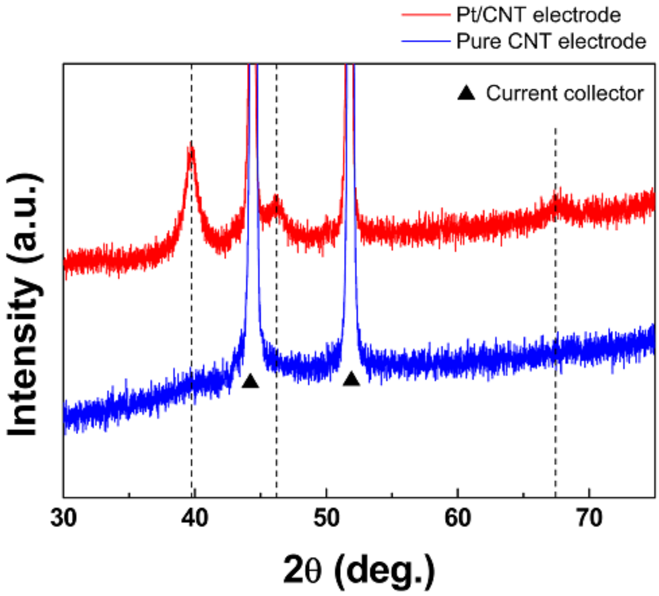


Figure S4. XRD results of the as-prepared CNT and Pt/CNT electrodes. The dash line corresponds to Pt.

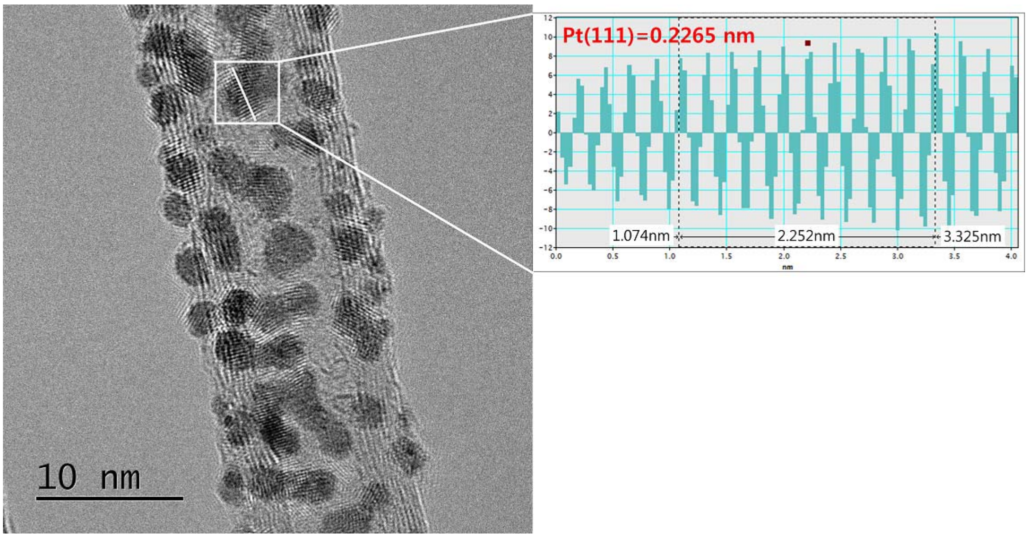


Figure S5. HR-TEM image of Pt/CNT and the d-spacing of the incorporated particle. The figure shows the average intervals of the incorporated particle (white line) is about 0.2252nm, which agrees well with the d-spacing between two adjacent lattice fringes of Pt (111) plane.

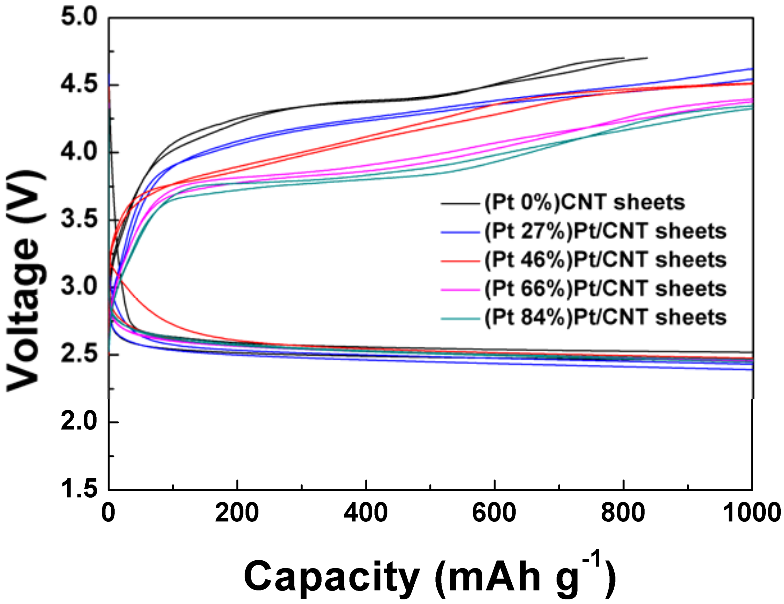


Figure S6. Electrochemical profiles of the PT/CNT electrodes at a current rate of 2,000 mA g^{-1} with the limited depth of discharge at 1000 mAh g^{-1} at different weight percentages of Pt. As the weight percentages of Pt increase, the polarization is gradually decreased. However, it should be noted that the catalytic activity of Pt is not obviously increased over 66 %.

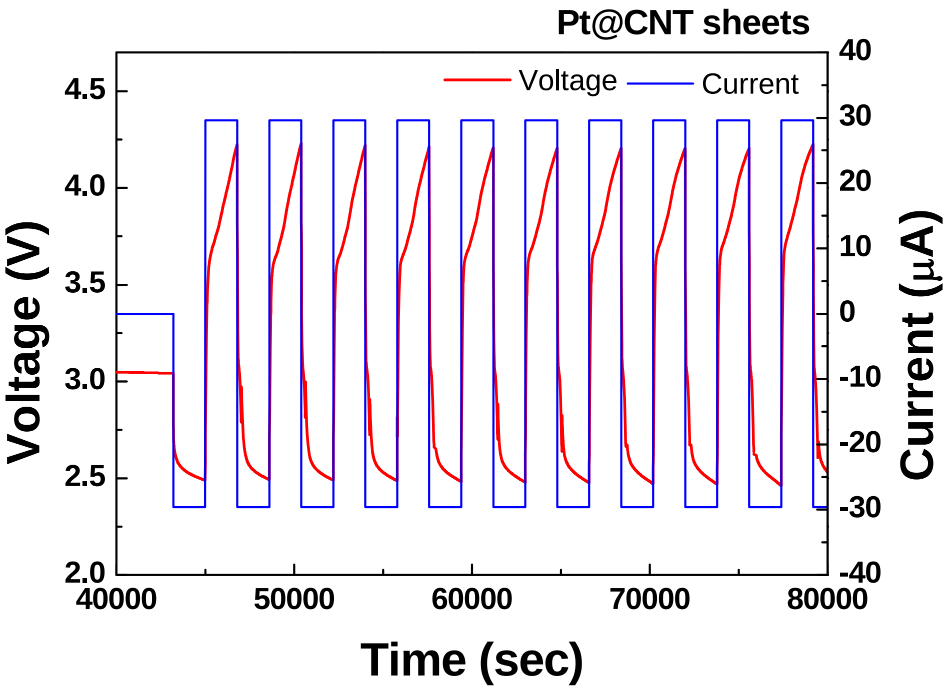


Figure S7. Time *vs.* voltage and current profiles of the first 10 cycles for the Pt/CNT electrode. Before the test, all of the cells were relaxed in an oxygen atmosphere for 12 h.

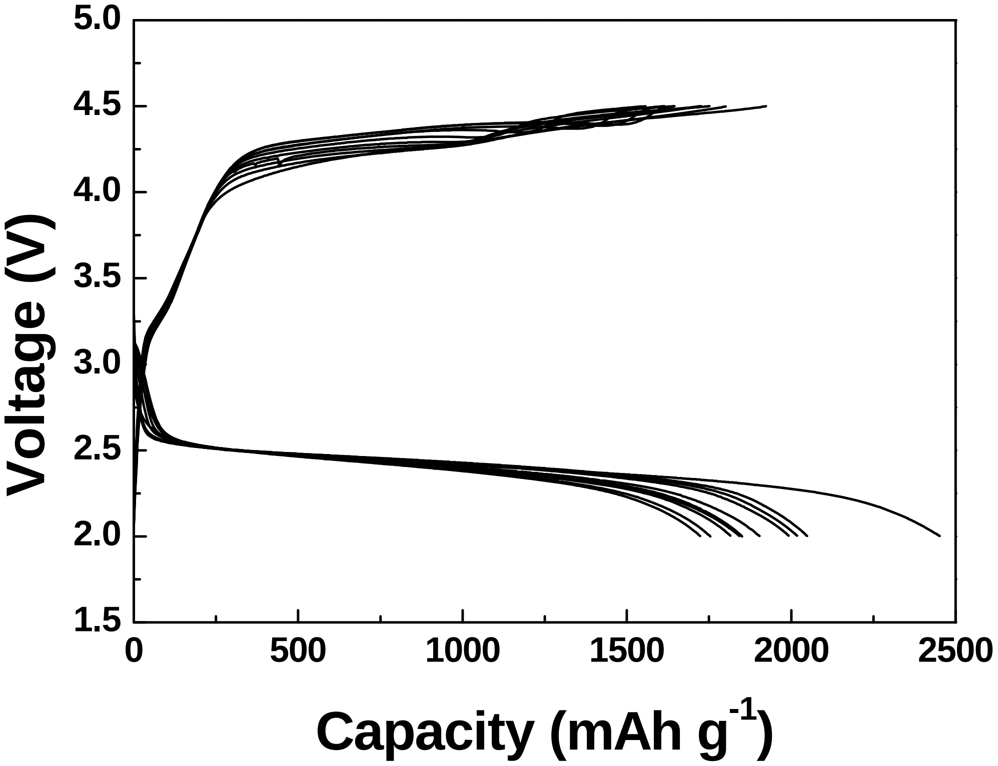


Figure S8. Discharge/charge profiles of the Pt/CNT electrode at 2000 mA g^{-1} with full discharge/charge between 2.0–4.5 V.

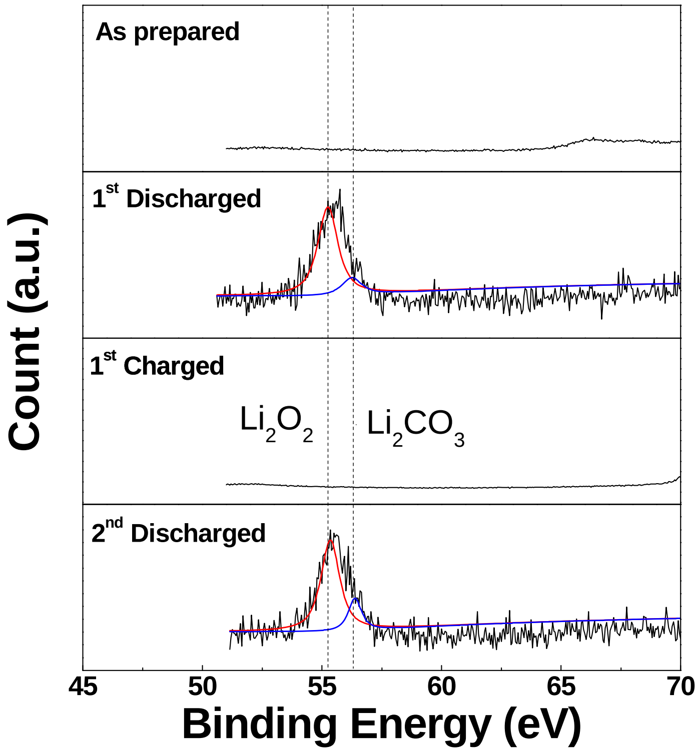


Figure S9. XPS spectra of Li 1s for the Pt/CNT electrode at each state. In the initial cycles, the major reaction product was Li_2O_2, while a small amount of Li_2CO_3 was also present.

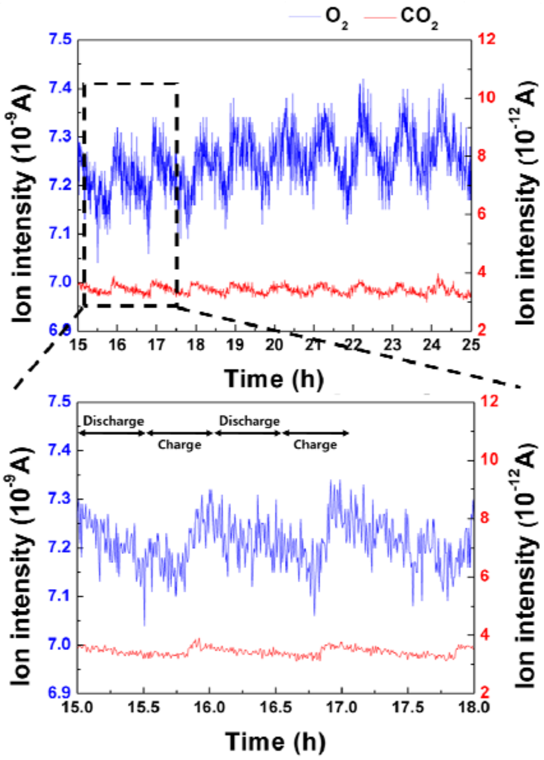


Figure S10. Gas (O_2 and CO_2) evolution results of the PT/CNT electrodes measured by DEMS. Each discharge and charge time is 30 minute.

Differential electrochemical mass spectrometry (DEMS) was carried out to investigate the gas consumption/evolution results. DEMS consists of a combination of a mass spectrometer (MS) (HPR-20, Hiden Analytical) and a potentio-galvanostat (WonA Tech, WBCS 3000, Korea). The gases that evolved during the discharge/charge process were swept into a MS upon the start of the electrochemical test. The flow rate of carrier gas (oxygen) swept into the MS is 0.5 cc/min.

During the discharge, the ion intensity of oxygen gradually decrease, which implies that the oxygen is used for the formation of discharge products. Almost same amount of oxygen is evolved during the charge implying the reversibility of the reaction. The theoretical volume of evolved/ consumed oxygen ($2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2$) is 0.01458 mL for the one cycle in our system. The average volume of the used oxygen is 0.01425 mL, which is well matched with the theoretical value. Also the average volume of CO_2 gas evolved during charge is only 5.2 % (0.00075 mL) compared to that of oxygen. Relatively small amount of CO_2 is evolved during charge. The detection of CO_2 gas means the existence of lithium carbonate, which is well corresponds to XPS, FT-IR and TEM in the manuscript. Small amount of lithium carbonate inevitably exist in the current Li-air batteries using carbon substrate and TEGDME electrolyte. It is partly decomposed during charge, however, some remains and gradually stacked during cycles, which deteriorates the cycle life of Li air cells.

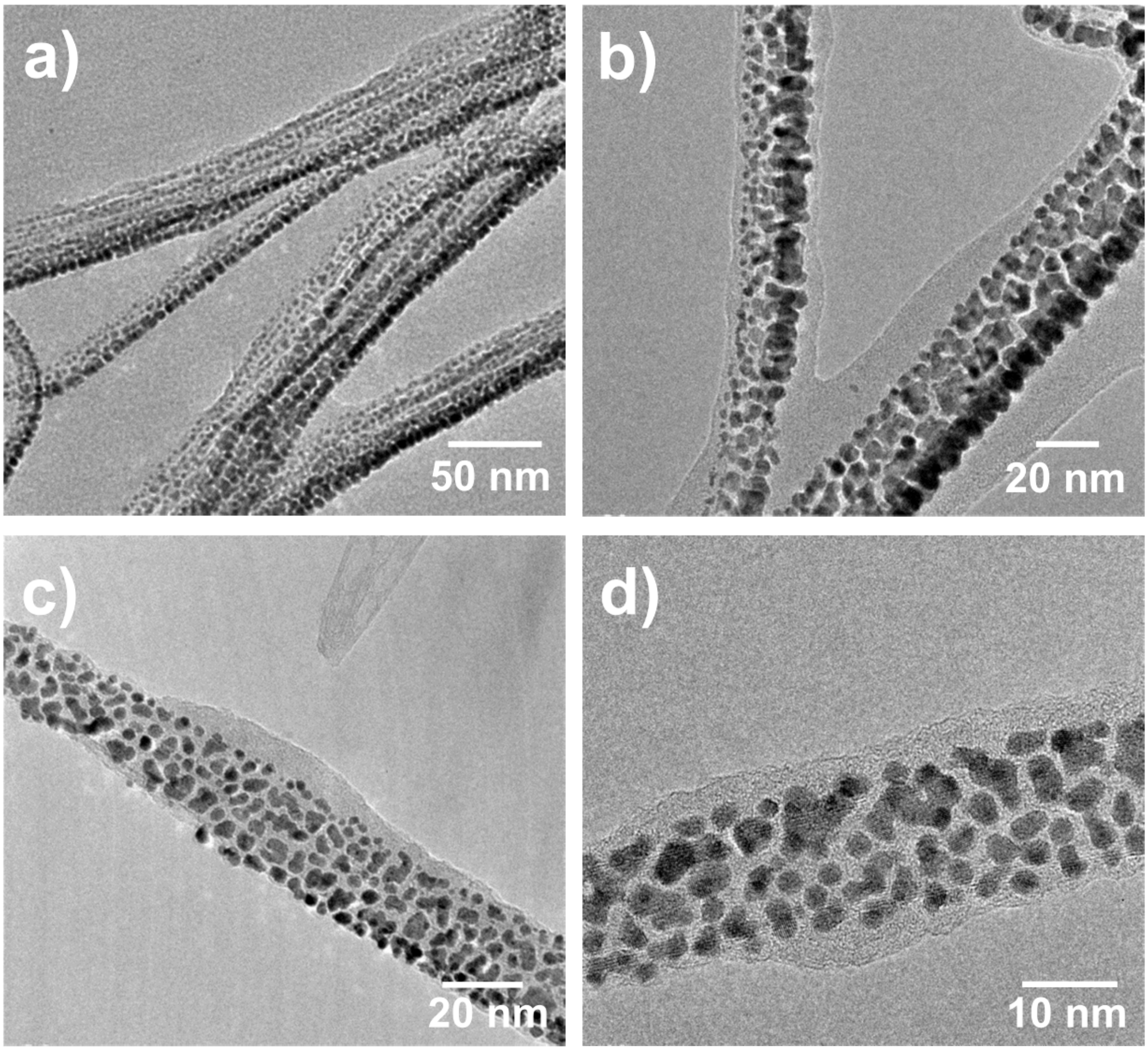


Figure S11. Various TEM images of the Pt/CNT electrode after the initial discharge to 1,000 mAh g^{-1}.

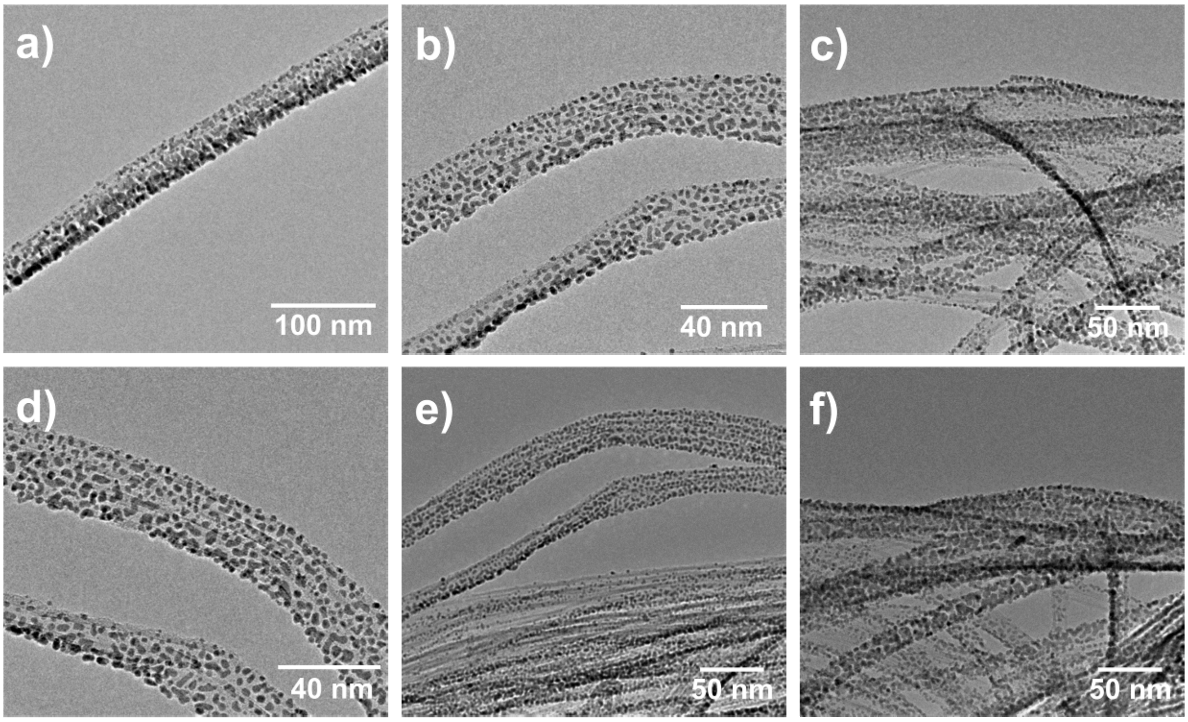


Figure S12. Various TEM images of the Pt/CNT electrode after the first charge. The discharge products were clearly decomposed and clean CNT surfaces were observed.

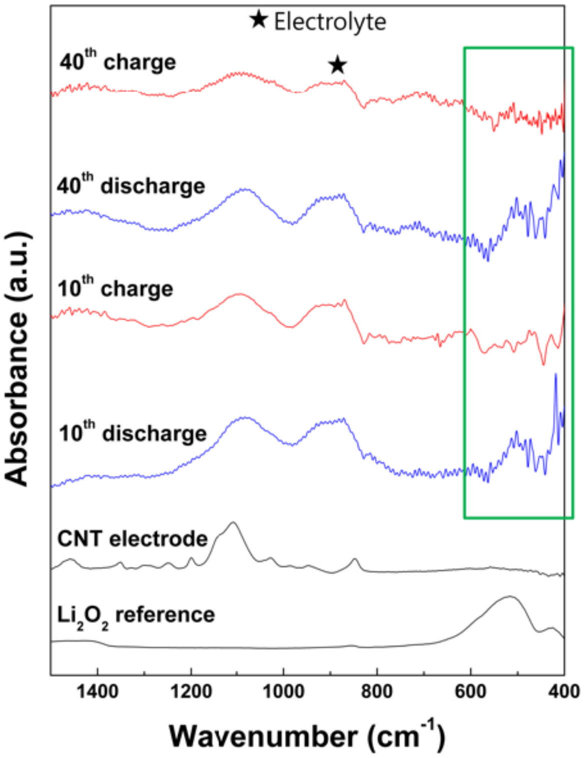


Figure S13. FT-IR measurement of air electrodes collected at 10th and 40th discharge/charge.

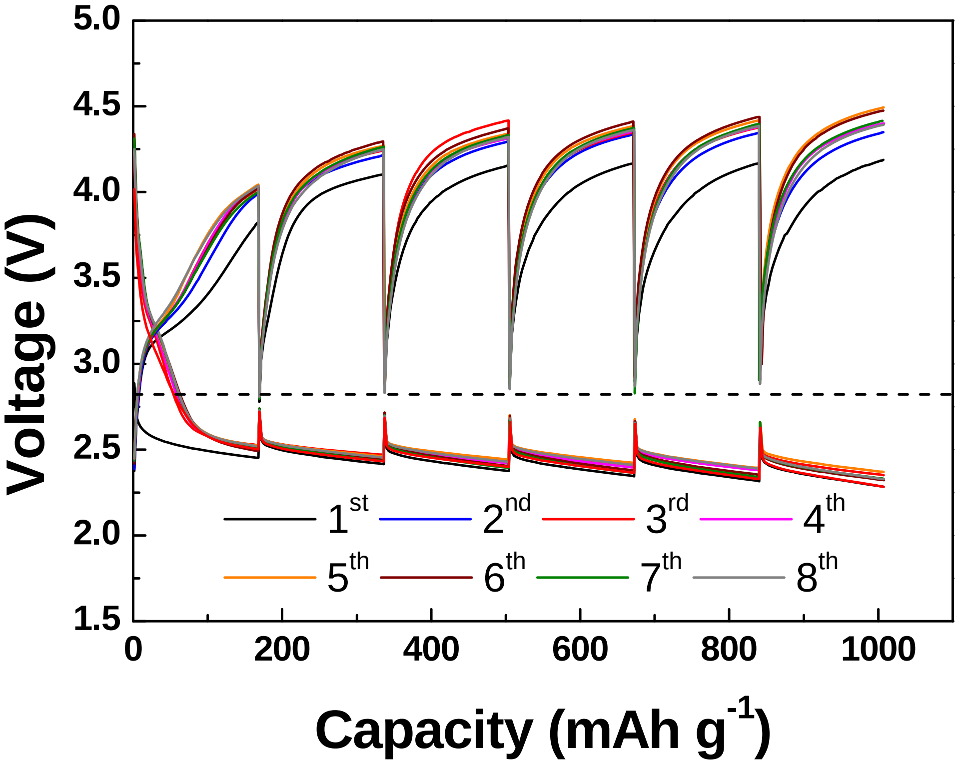


Figure S14. (a) GITT voltage profiles of the Pt/CNT electrode. During discharge/charge, the relaxation potential at each step approached the theoretical formation potential of Li_2O_2 (2.96 V).

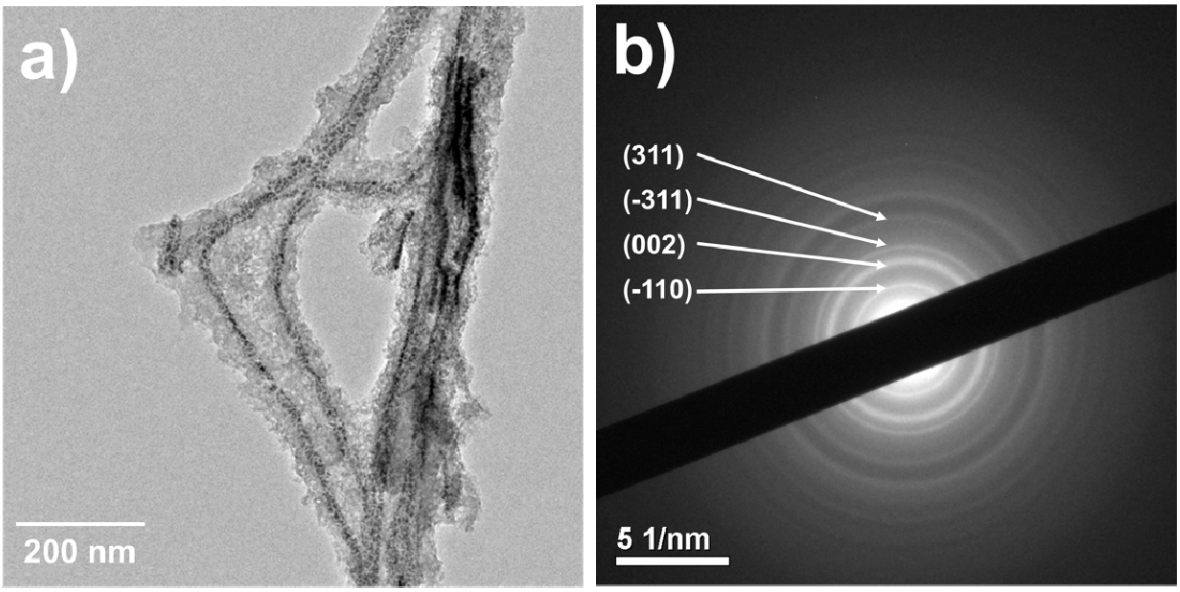


Figure S15. (a) TEM image of the Pt/CNT electrode at the end of cycles. (b) The corresponding diffraction pattern proves the formation of Li_2CO_3 at the surface of Pt/CNT electrode.

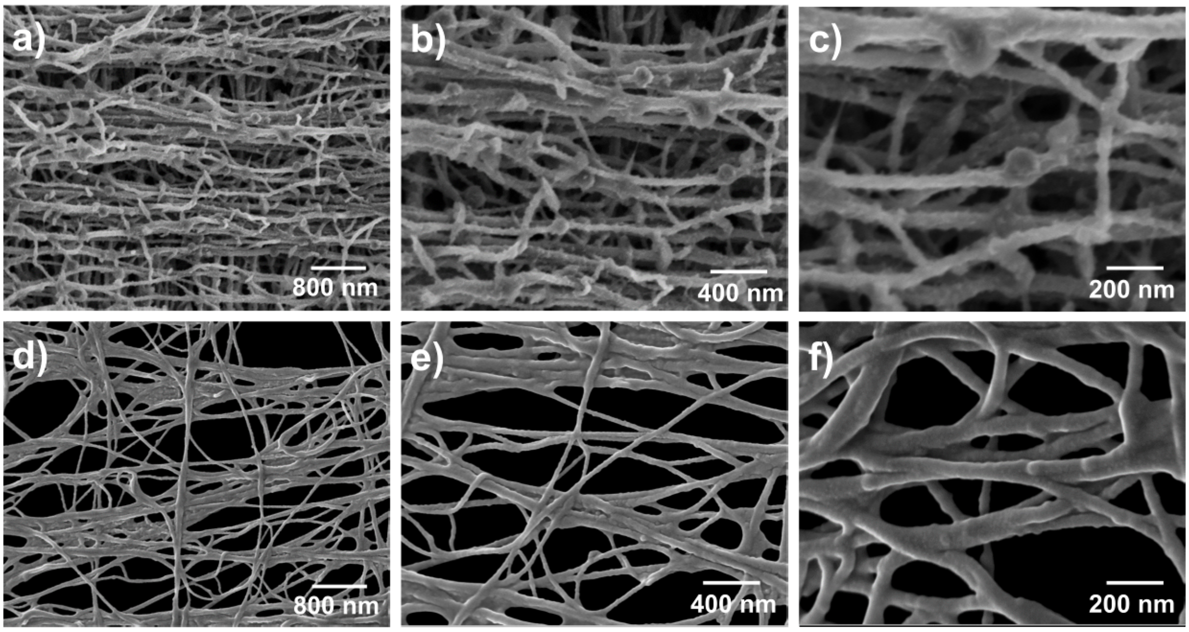


Figure S16. SEM images at various magnifications of (a–c) the CNT electrode without catalyst and (d–f) the Pt/CNT electrode after the first discharge to 2.0 V.

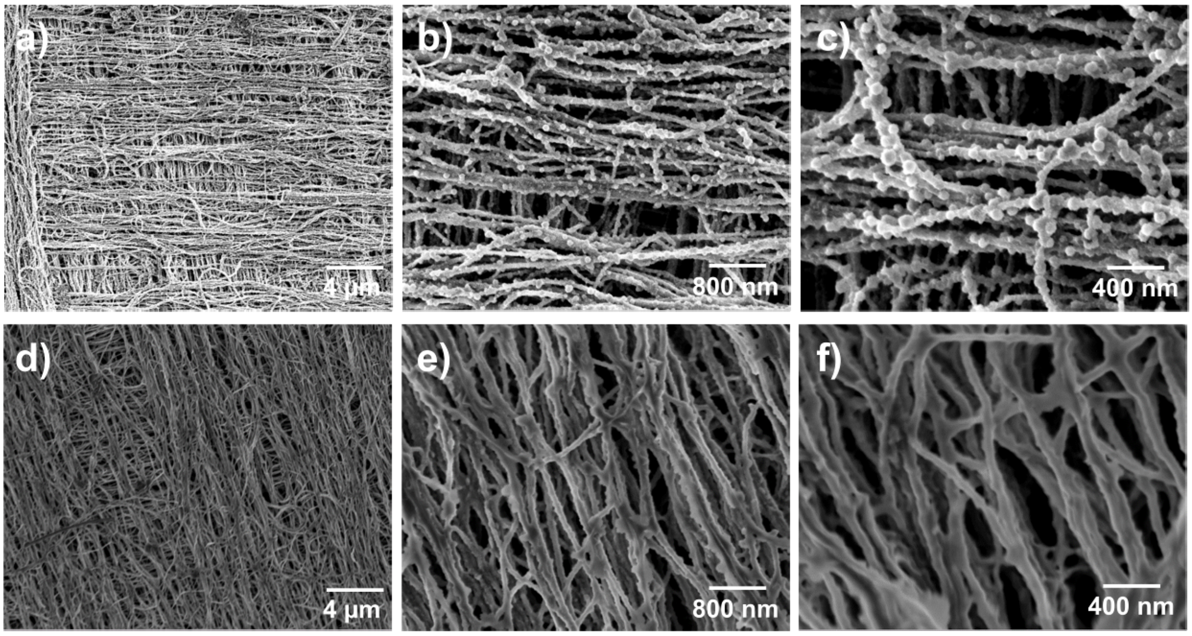


Figure S17. SEM images at various magnifications of (a–c) the CNT electrode without catalyst and (d–f) the Pt/CNT electrode at the end of cycles (30 and 100 cycles, respectively).