Supporting Information

Real-Time Imaging of the Electrochemical Process in Na-O_2 Nanobatteries Using Pt@CNT and $Pt_{0.8}Ir_{0.2}$@CNT Air Cathodes

Yuanmin Zhu[a,b], Fei Yang [a], Mohan Guo[c], Lang Chen[c] and Meng Gu[a]*

[a]Department of Materials Science and Engineering, and Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen 518055, China

[b]SUSTech Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen 518055, China

[c]Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China

Content:

1. Description of Supplementary Movies

Movie S1.avi

In situ TEM movie showing the morphological evolution of a Pt deposited carbon nanotube (Pt@CNT) cathode against Na in an O_2 environment during discharging and charging. The movie S1was recorded at 2 frames/second and is played at 30× speed.

Movie S2.avi

Morphology evolution of a Pt@CNT oxygen cathode during the discharge process of a Na-O2 nanobattery in (a) sodiation on CNT and (b) Na-O2 reaction upon a -0.5V bias. The movie S2 was recorded at 2 frames/second and is played at 10× speed.

Movie S3.avi

Real time *in situ* experiments of Na-Pt@CNT nanobettery without oxygen environment and only found that the Na ions go through the CNT, leading the volume expansion. No bubble-like morphology was observed during the electrochemical process. The movie S3 was recorded at 2 frames/second and is played at 45× speed.

Movie S4.avi

Time-resolved multiple cycles of the Na-O2 nanobatteries at the same reaction area in Movie S1 were performed by *in situ* TEM. The movie S4 was recorded at 2 frames/second and is played at 45× speed.

Movie S5.avi

Time-resolved *in situ* TEM movie shows the morphological evolution of the $Pt_{0.8}Ir_{0.2}$@CNT cathode against Na in an O_2 environment during discharge and charging processes. The movie S4 was recorded at 1 frames/second and is played at 30× speed.

Movie S6.avi

Real time *in situ* SAEDPs to explore structural information on the phase evolution during the discharging and charging processes. The movie S6 was recorded at 1 frames/second and is played at 20× speed.

Movie S7.avi

Movie S7 shows the corresponding morphological evolution of the $Pt_{0.8}Ir_{0.2}$@CNT cathode monitored in Movie S6. The movie S7 was recorded at 1 frames/second and is played at 30× speed.

2. Supplementary Figures

2.1 Microstructure of the Pt@CNTs

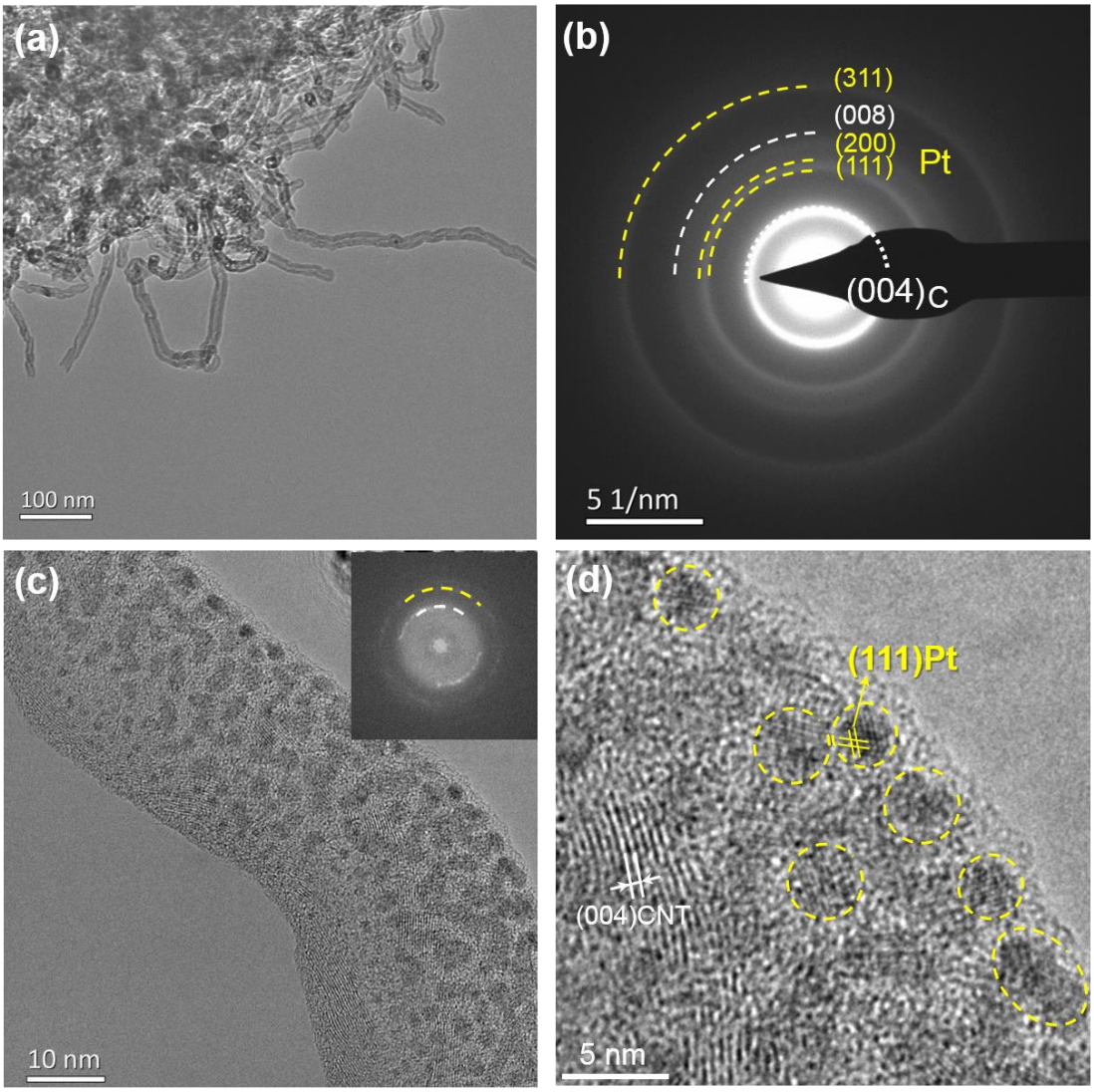

Figure S1 The microstructure of the pristine Pt doped carbon nanotubes (Pt@CNTs). (a) Transmission electron microscopy (TEM) image of the pristine Pt@CNTs glued on the half grid and the corresponding selected area electron diffraction patterns (EDPs). (b). High resolution TEM images shows the distribution of Pt nanoparticles on the CNT surface (c) and the lattices of Pt particles and CNT (d).

2.2 Morphology evolution of a Pt@CNT cathode during discharge

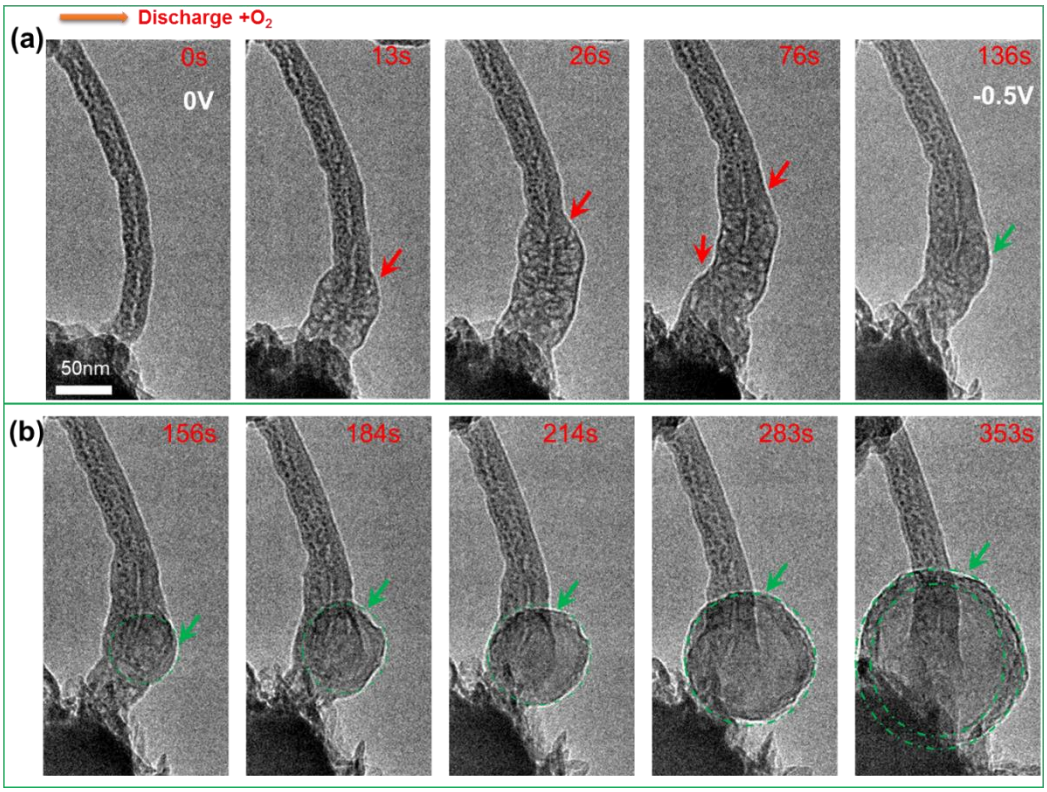

Figure S2 Morphology evolution of a Pt@CNT oxygen cathode during the discharge process of a Na-O_2 nanobattery in (a) spontaneously sodiation on CNT and (b) Na-O_2 reaction upon a -0.5V bias accompany with a bubble-like structure appeared. The reaction areas are pointed out by arrows.

2.3 Comparison experiment of Na and Pt@CNT without O_2

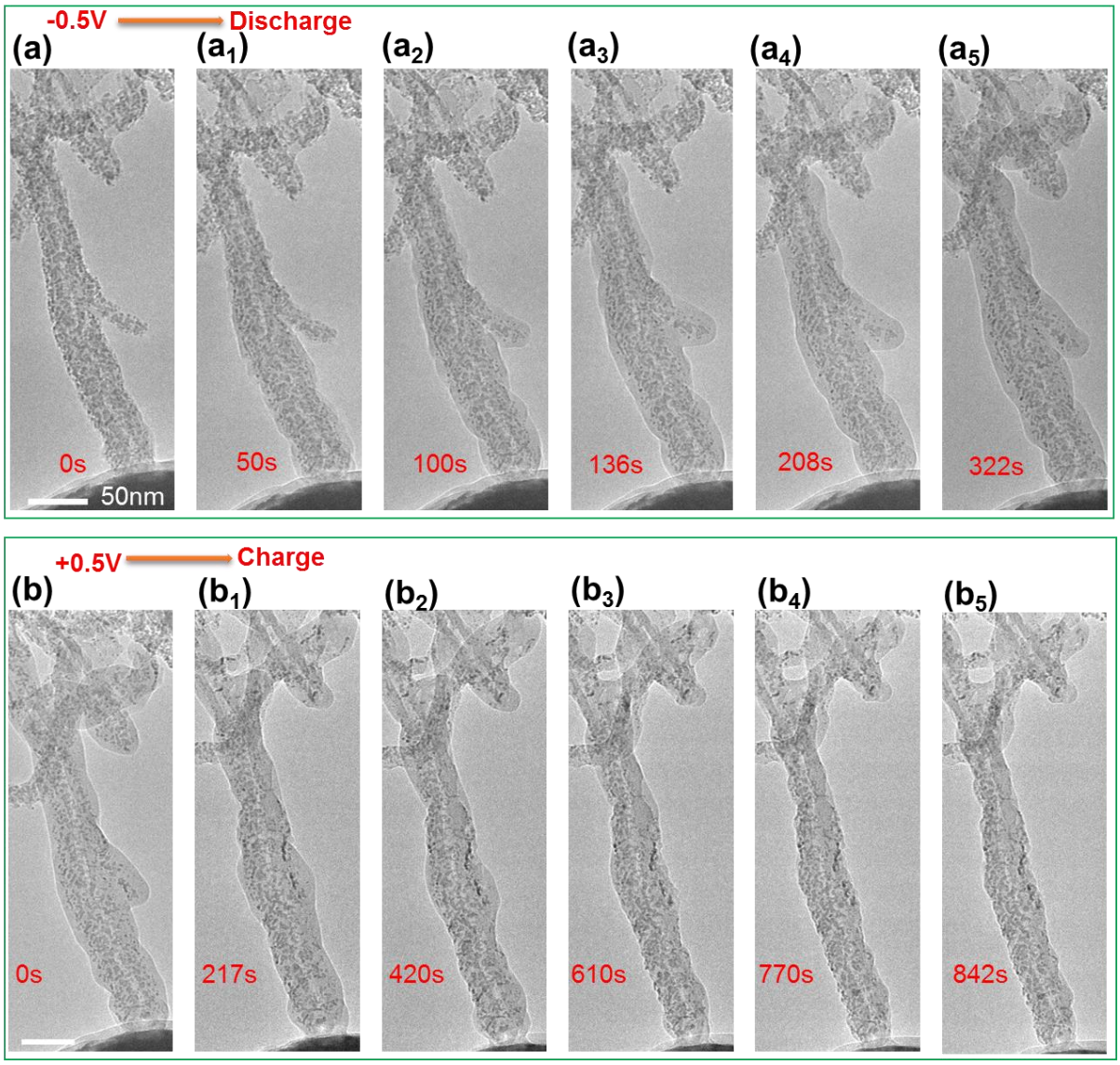

Figure S3 The Sodiation-Desodiation cycle of Pt@CNT without oxygen environment for comparison. (a) Discharging at -0.5V; (b) Charging at +0.5V.

2.4 NaO_2 decompositions without e-beam exposure

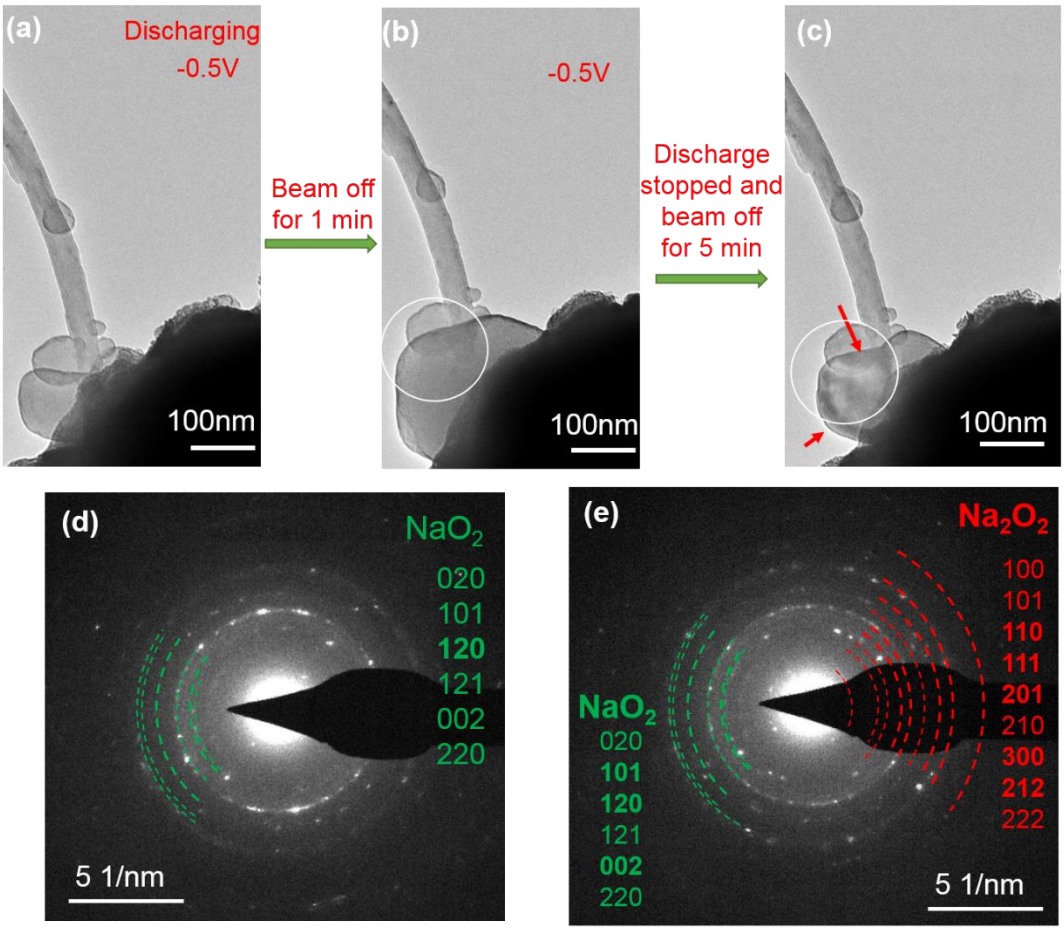

Figure S4 TEM morphologies evolution of the Na-O_2 cell discharging without electron beam exposure. The e-beam opened only when images were acquired at (a) 0 min (b) 1min and (c) 6min. (d) The corresponding SAED patterns from the white circled area in (b). (e) The corresponding SAED patterns from circled area in (c).

2.5 Microstructures of the as synthesized $Pt_{0.8}Ir_{0.2}$@CNTs

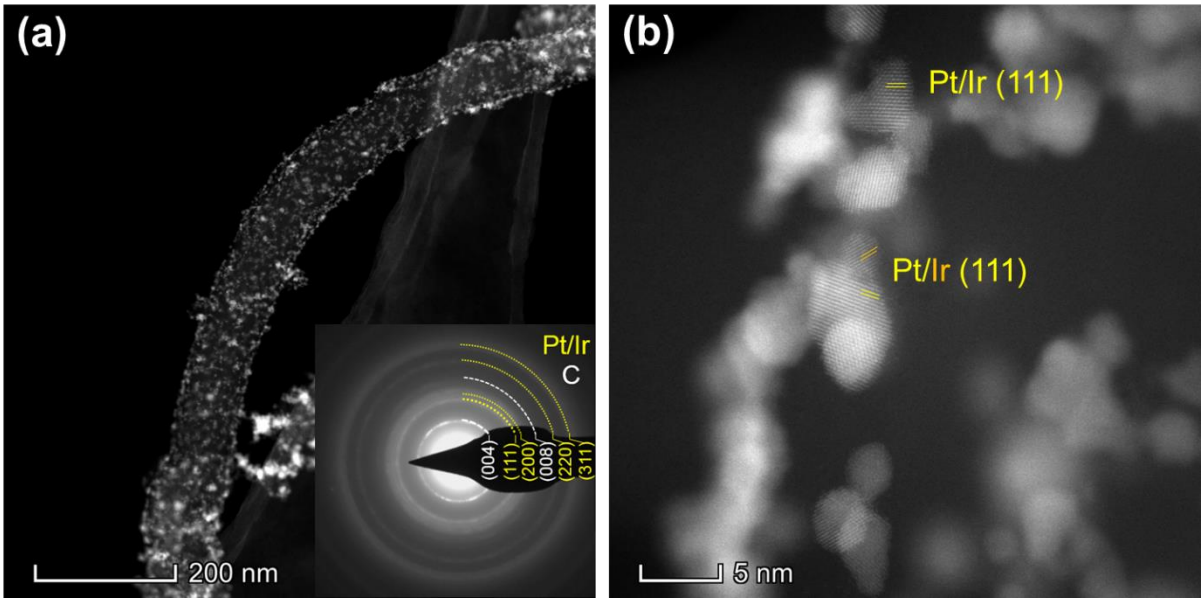

Figure S5 microstructure of the synthesized $Pt_{0.8}Ir_{0.2}$@CNT. (a) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image showing homogeneously distributed Pt/Ir bimetallic catalysts on CNT. (b) High resolution STEM investigation gives further insight of the Pt/Ir catalysts.

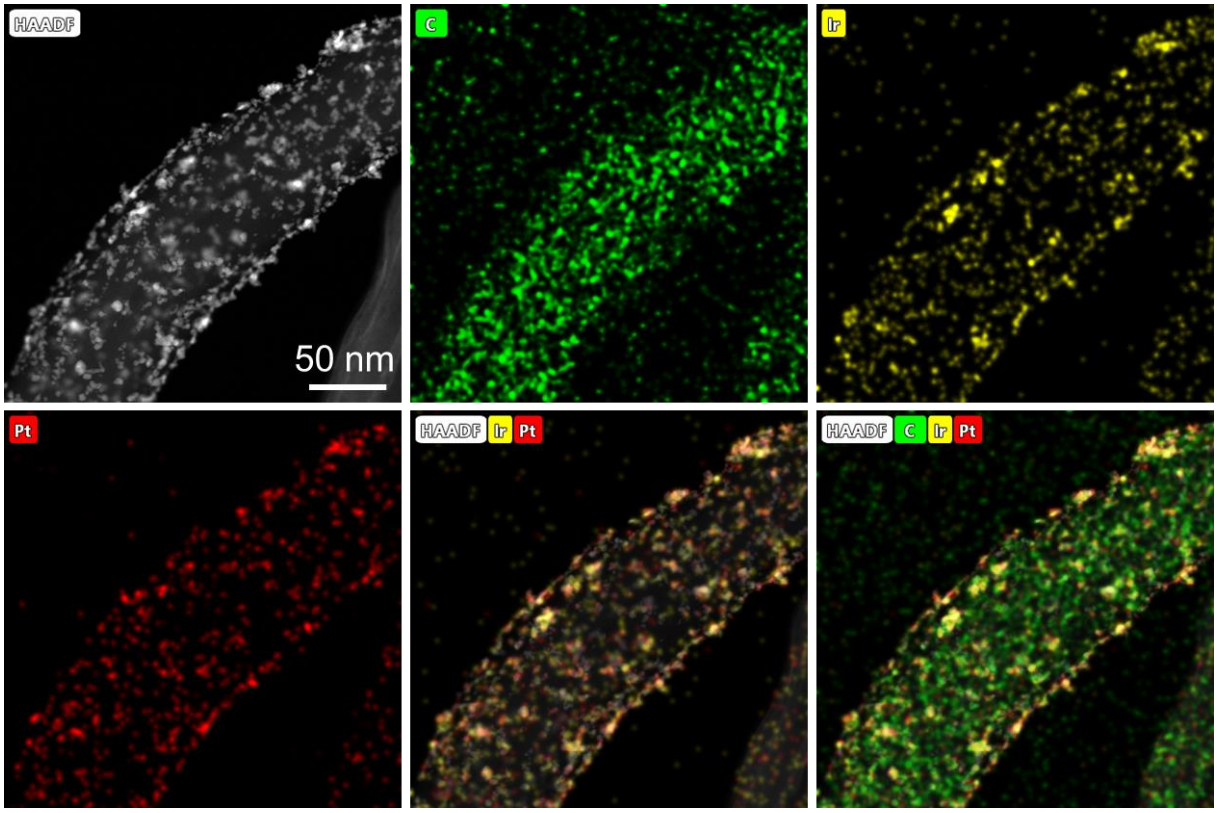

Figure S6 High resolution STEM-EDS mapping of $Pt_{0.8}Ir_{0.2}$@CNT demonstrating the compostion of the Pt/Ir nanoparticales. (a) HAADF image; (b) C map; (c) Ir map; (d) Pt map; (e) overlapping maps of Pt, Ir; (f) overlapping maps of C, Pt, Ir.

2.6 Comparison experiment of Na-O_2 on pure CNTs

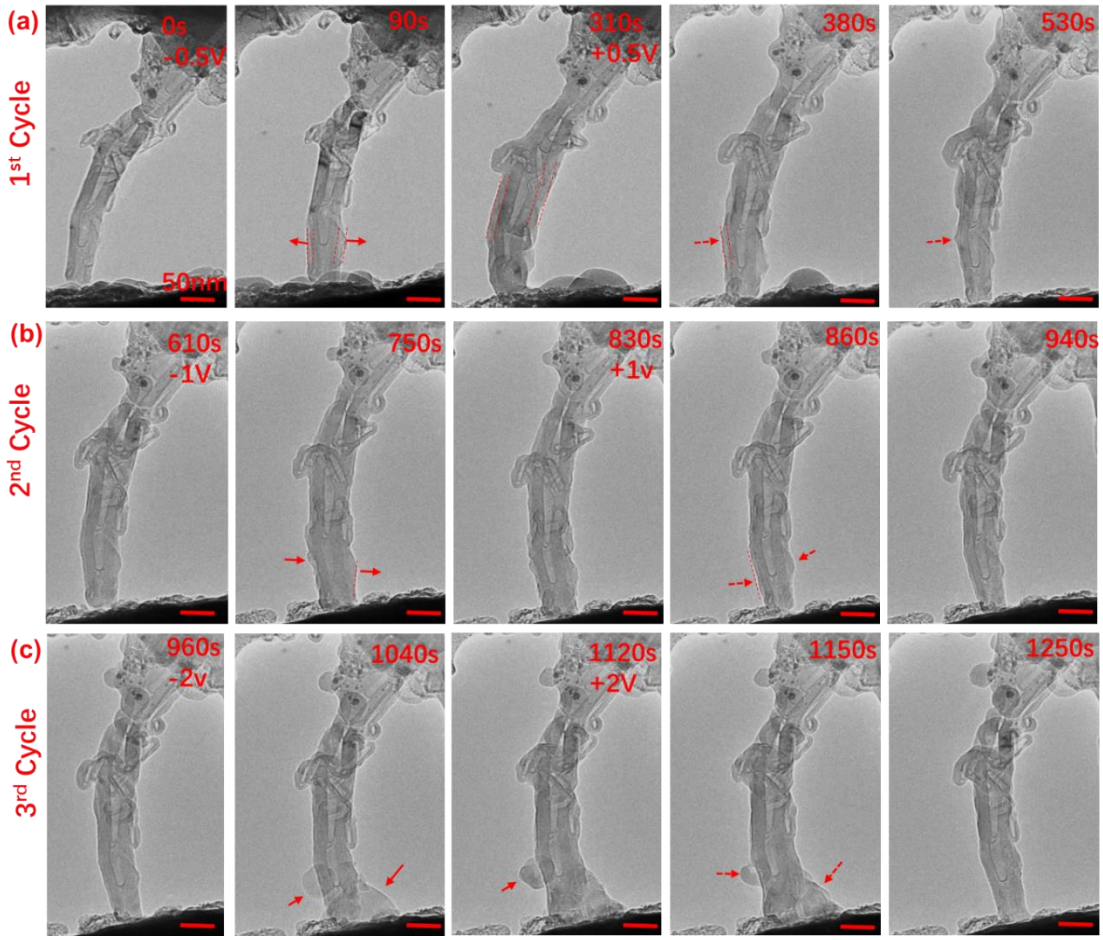

Figure S7 Real-time *in situ* TEM images depict the morphological evolution during the discharging and charging process of a pure CNT air cathode without catalyst against Na metal anode in O2 environment with the first 3 cycles shown in (a) 1st cycle, (b) 2nd cycle and (c) 3rd cycle. At the 3rd cycle, the Na-O_2 reaction happened combining with the Na_2O_2 nanospheres formation and decomposition under a relative high bias voltage.

2.7 *In situ* TEM of a $Pt_{0.8}Ir_{0.2}$@CNT cathode during cycling

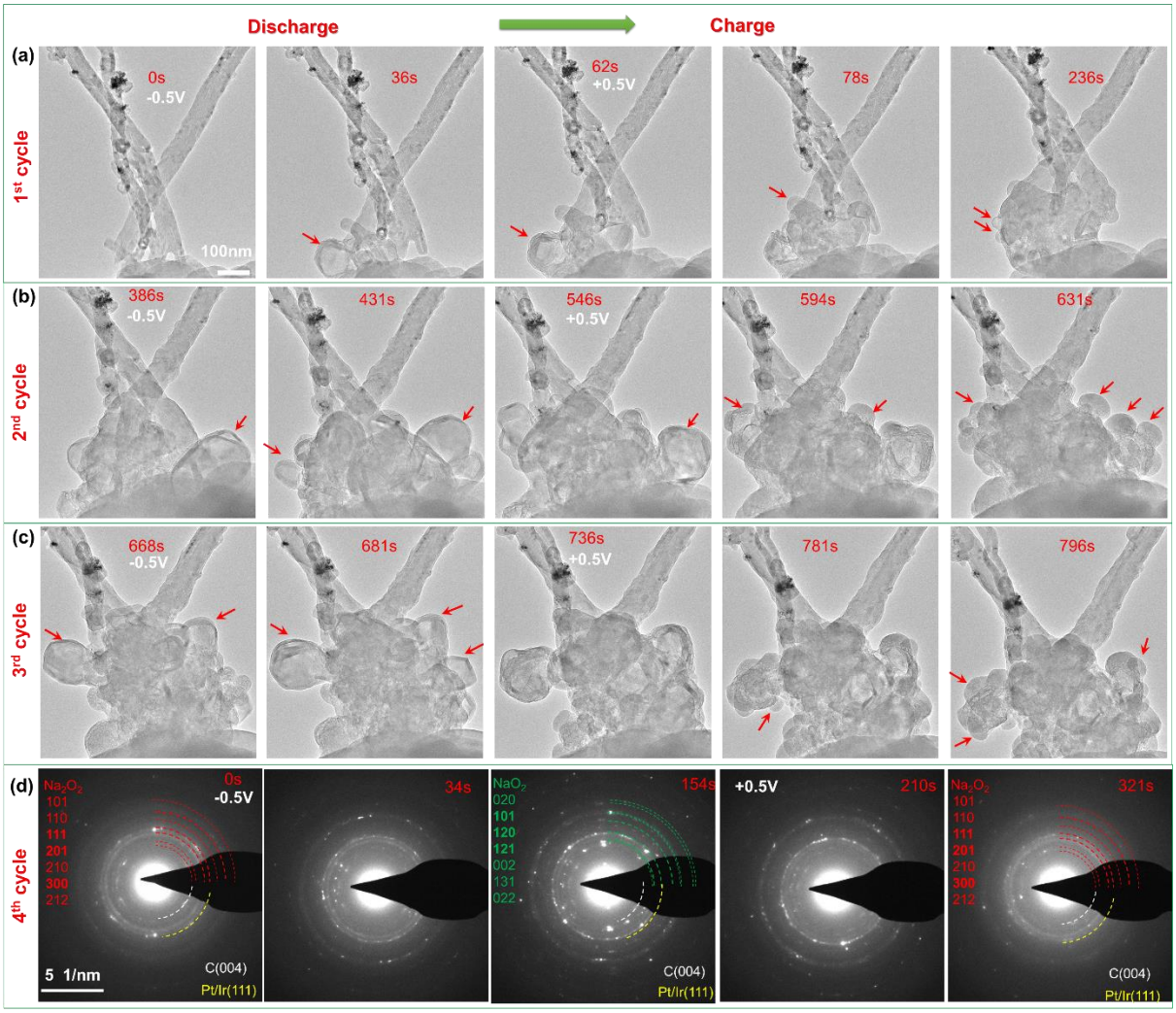

Figure S8 Time-resolved *in situ* TEM images illustrate the morphological evolution of a $Pt_{0.8}Ir_{0.2}$@CNT cathode during discharge and charging against Na in an O_2 environment. Morphology evolution of the Na-O_2 nanocell during the first (a), second (b), and third cycle. (d) The real-time evolution of EDPs at the same reaction area during the fourth cycle.

2.8 STEM-EDS mapping of a $Pt_{0.8}Ir_{0.2}$@CNT after discharging

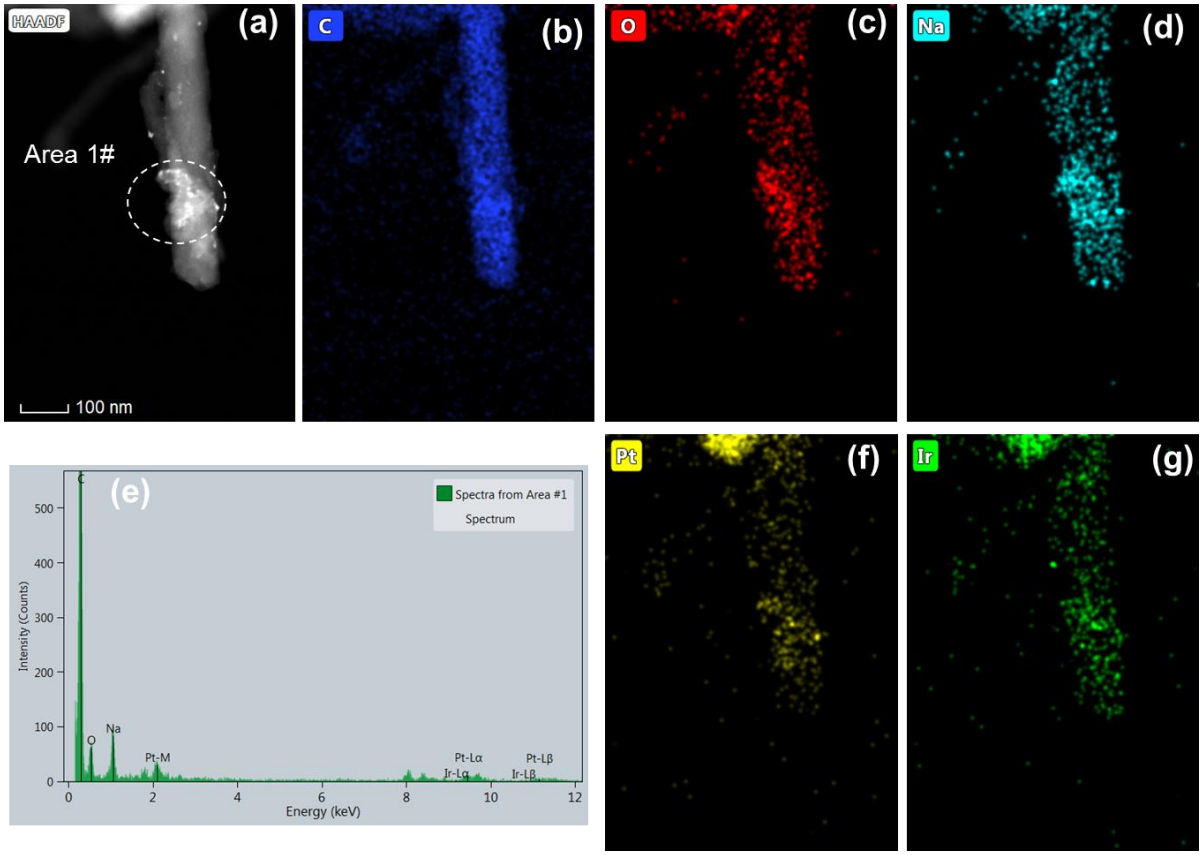

Figure S9 STEM-EDS mapping of a $Pt_{0.8}Ir_{0.2}$@CNT after discharging process as a Na-O2 cell. (a) HAADF image; (b) C map; (c) O map; (d) Na map (e) EDS spectrum from the area 1# in (a), (f) Pt map; (g) Ir Map.

2.9 Typical *in situ* I-V curves and EIS

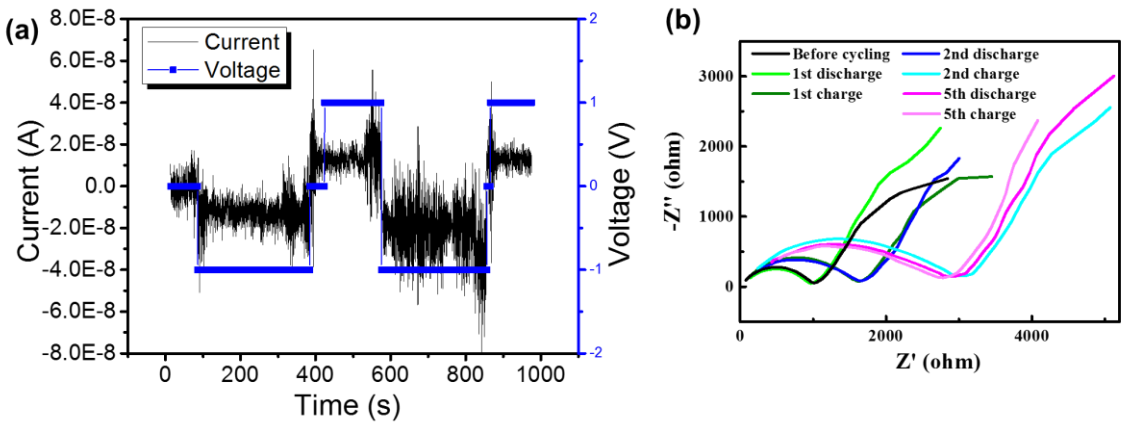

Figure S10 (a) The typical voltage and current density curves v.s. time during the discharging and charging cycles. (b) Electrochemical impedance spectrum (EIS) of Na-O_2 liquid cells with the Pt/Ir@CNT cathode.

2.10 *In situ* TEM experiments at low beam voltage and dose

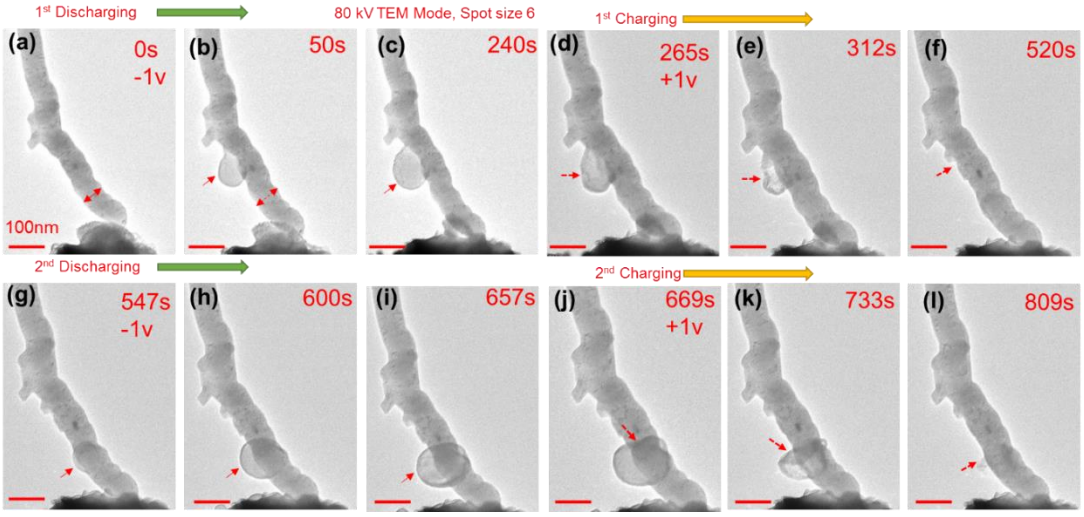

Figure S11 Real-time *in situ* low beam voltage (80 kV) TEM images depict the morphological evolution during the discharging and charging process of a $Pt_{0.8}Ir_{0.2}$CNT air cathode against Na metal anode in O_2 environment. (a-f) 1st cycle, (g-l) 2nd cycle. The spot size was set as 6 to decrease the electron beam effect on the samples and beam screen current is controlled below 0.1 nA.

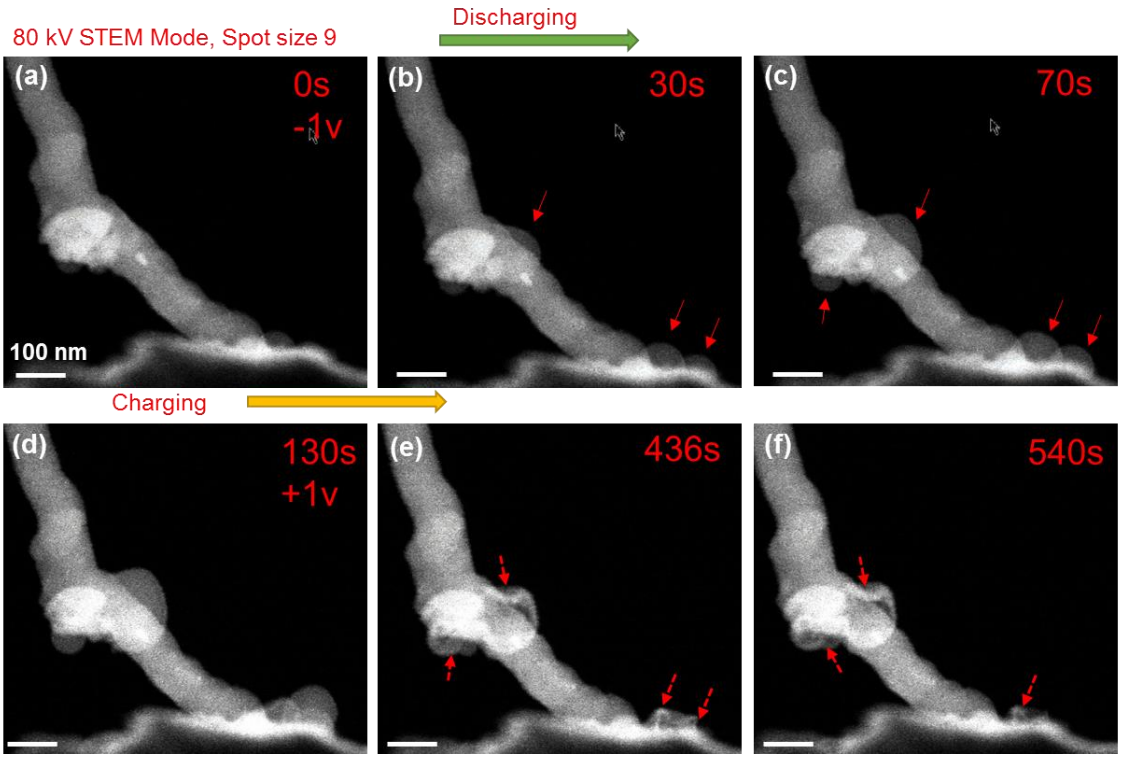

Figure S12 Real-time *in situ* low beam voltage (80 kV) STEM images show the morphological evolution during the discharging and charging process of a $Pt_{0.8}Ir_{0.2}$CNT air cathode against Na metal anode in O_2 environment. (a-c) Discharging, (d-f) Charging. The spot size was set as 9 to decrease the electron beam effect on the samples. In STEM mode, the e-beam effect is minimized as we only took images intermittently.