ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201102200

Nitrogen-Doped Carbon Nanotube Composite Fiber with a Core–Sheath Structure for Novel Electrodes

*Tao Chen , Zhenbo Cai , Zhibin Yang , Li Li , Xuemei Sun , Tao Huang , Aishui Yu , Hamid G. Kia , and Huisheng Peng **

Supporting Information

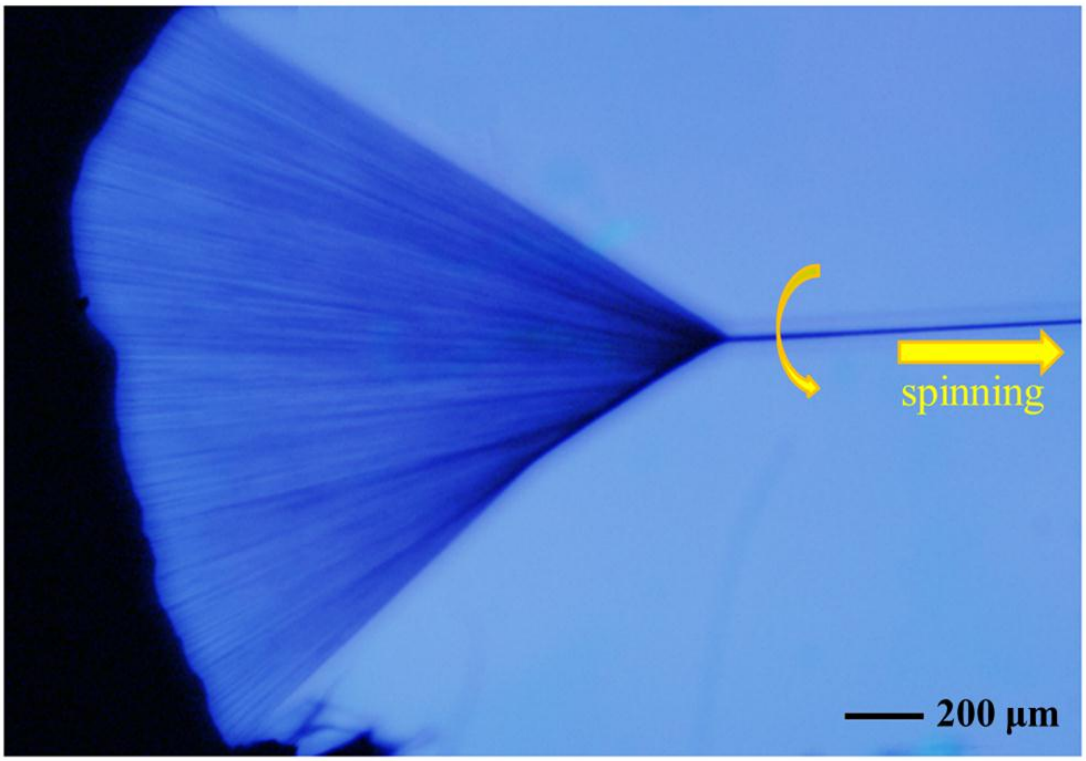

Figure S1. Optical micrograph of the spinning process to obtain a CNT fiber from a CNT array through a rotating probe. The left curved arrow shows the rotating direction during the spinning.

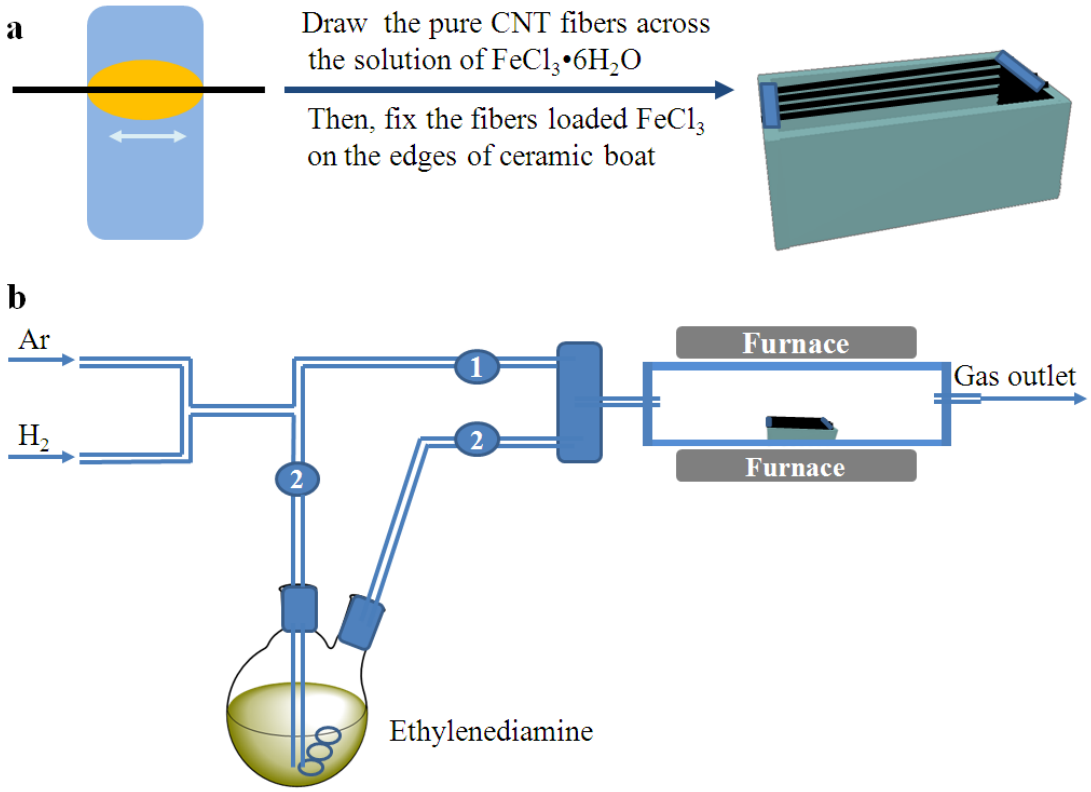

Figure S2. a) Schematic illustration for the preparation of $FeCl_3$ catalyst on the CNT fibers to grow NCNTs on their outer surfaces; b) Experimental setup for synthesis of NCNTs on the pure CNT fibers. Here "1" and "2" represent different channels for the gas flow. At the beginning of the synthesis, Channel 1 was turned on to induce the production of catalytic iron nanoparticles, while Channel 2 was turned off. After about 40 min Channel 1 was turned off while Channel 2 was turned on to grow NCNTs.

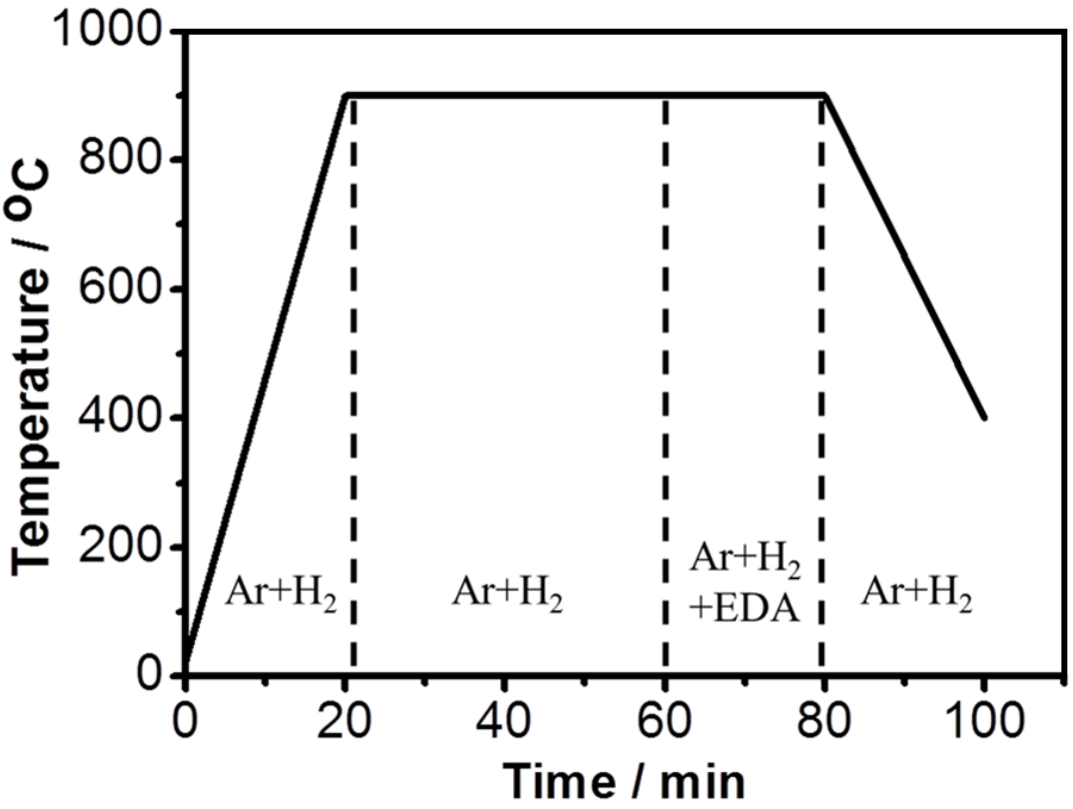

Figure S3. Temperature distribution during the growth of NCNTs (EDA represents ethylenediamine).

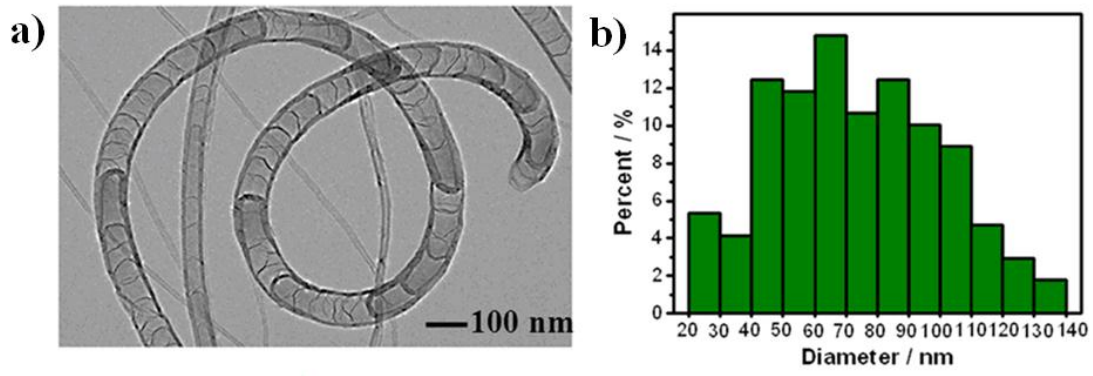

Figure S4. a) TEM image of NCNTs; **b)** The diameter distribution of NCNTs calculated from TEM images. Note that the smaller linear CNTs at **a** are undoped CNTs coming for the core part of composite fiber.

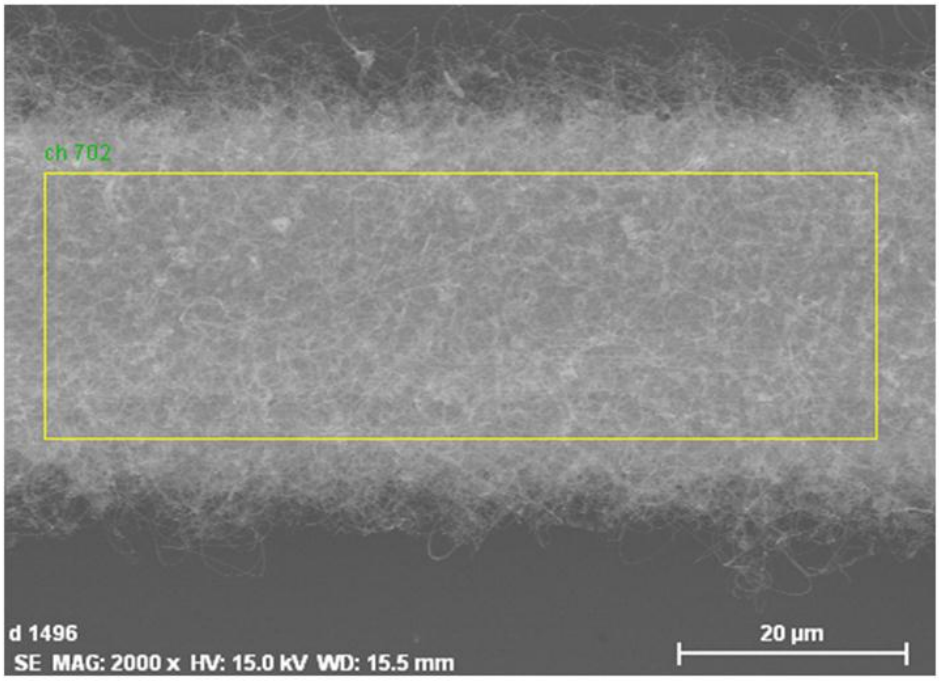

Figure S5. SEM image of a typical area used for energy-dispersive X-ray spectroscopy analysis of composite fiber.

Table S1. Summary of the elemental contents in NCNTs obtained from energy-dispersive X-ray spectroscopy. Eight different areas in two composite fibers were analyzed to produce the average values of elemental contents. The N content ranges from 4.7 to 6.0, and a trace of iron was also detected here.

Sample number	C atom / %	N atom / %	O atom / %	Fe atom / %
N1	86.9	4.7	8.4	0.03
N2	84.6	5.7	9.7	0.06
N3	86.4	5.5	8.1	0.05
N4	85.8	5.2	9.0	0.02

Table S2. Summary of the Raman characterizations for pure CNT fibers (P1-P4) and composite NCNT fibers (N1-N4). The average intensity ratio of D-band to G-band (I_G/I_D) for pure CNT fibers is 0.62, and the average I_G/I_D rises to 0.77 for composite NCNT fibers. That is, the defects increase after incorporation of nitrogen atoms into the graphitic layers in CNTs.

Sample number	I_D	I_G	I_D/I_G
P1	11165	16716	0.67
P2	10882	20026	0.54
P3	9117	14677	0.62
P4	11472	17691	0.65
N1	3731	4435	0.84
N2	3456	4699	0.74
N3	1606	2174	0.74
N4	4378	5907	0.74

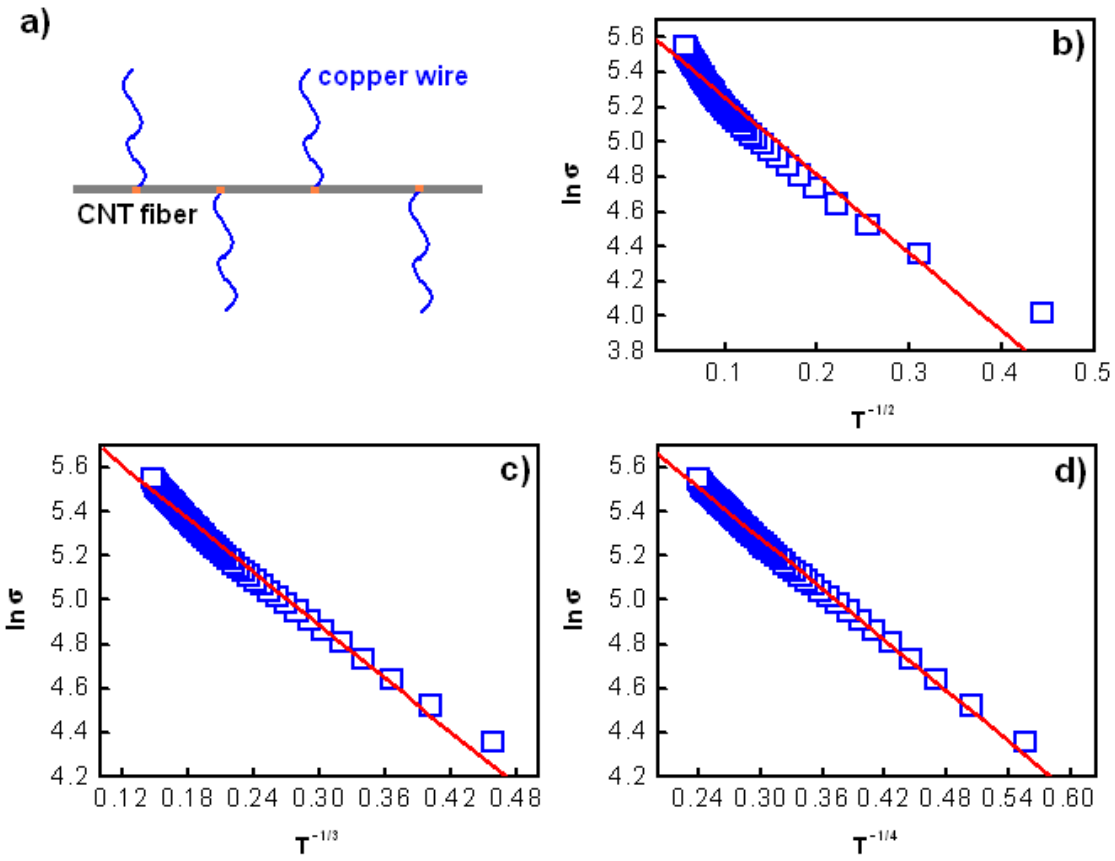

Figure S6. Scaling of electrical conductivity (σ) with temperature (T) according to the equation of $\sigma \propto \exp(-A/T[1/(d+1)])$ based on the Mott's hopping model, where *A* is a constant and *d* is the dimensionality. a) Schematic illustration to the measurement based on a four-probe method. b) The plot of lnσ versus $T^{-1/2}$ (for $d = 1$) with linear fitting coefficient of 0.927. c) The plot of lnσ versus $T^{-1/3}$ (for $d = 2$) with linear fitting coefficient of 0.971. d) The plot of lnσ versus $T^{-1/4}$ (for $d = 3$) with linear fitting coefficients of 0.981. The results indicate that the electron transport of CNT fibers is consistent with a three-dimensional hopping mechanism (*Adv. Mater.* 2007, 19, 3358).

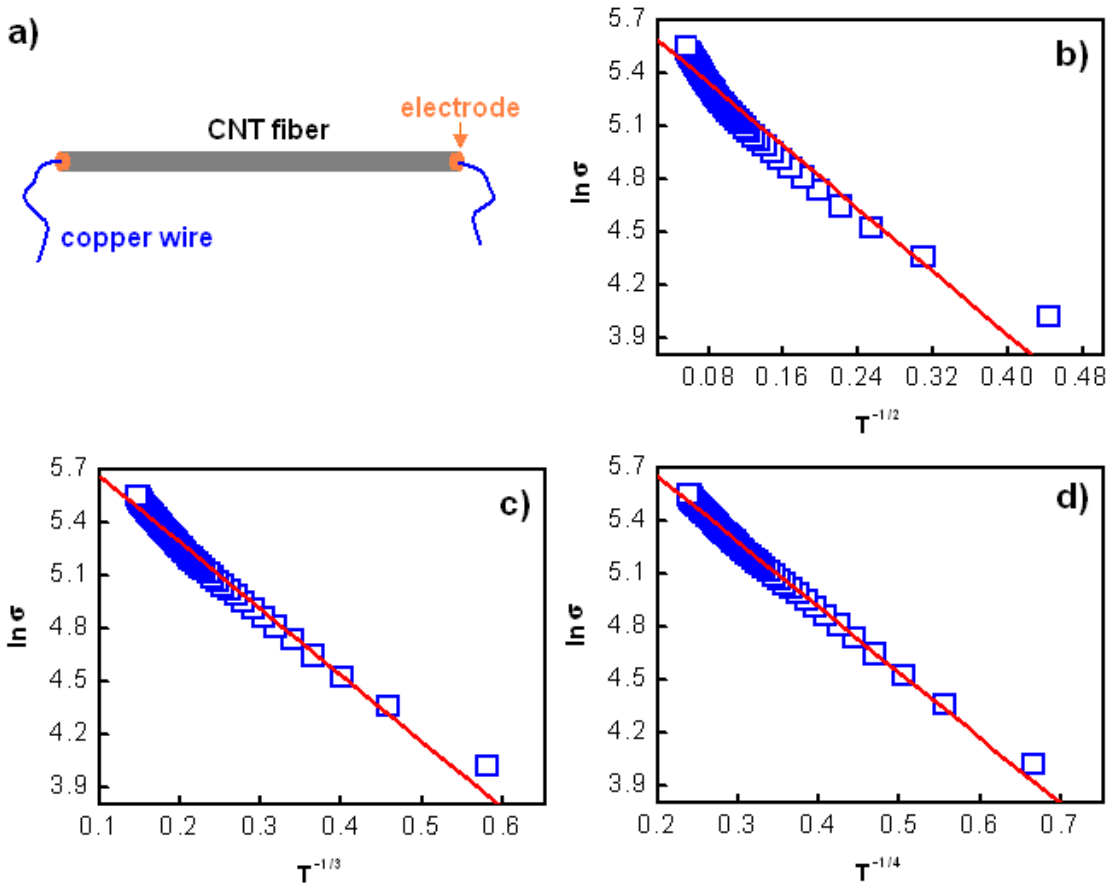

Figure S7. Scaling of electrical conductivity (σ) with temperature (T) according to the equation of $\sigma \propto \exp(-A/T[1/(d+1)])$ based on the Mott's hopping model, where *A* is a constant and *d* is the dimensionality. a) Schematic illustration to the measurement based on a two-probe method. b) The plot of lnσ versus $T^{1/2}$ (for $d = 1$) with linear fitting coefficient of 0.927. c) The plot of lnσ versus $T^{1/3}$ (for $d = 2$) with linear fitting coefficient of 0.960. d) The plot of lnσ versus $T^{1/4}$ (for $d = 3$) with linear fitting coefficients of 0.976. The results also indicate that the electron transport of CNT fibers is consistent with a three-dimensional hopping mechanism (*Adv. Mater.* 2007, 19, 3358).

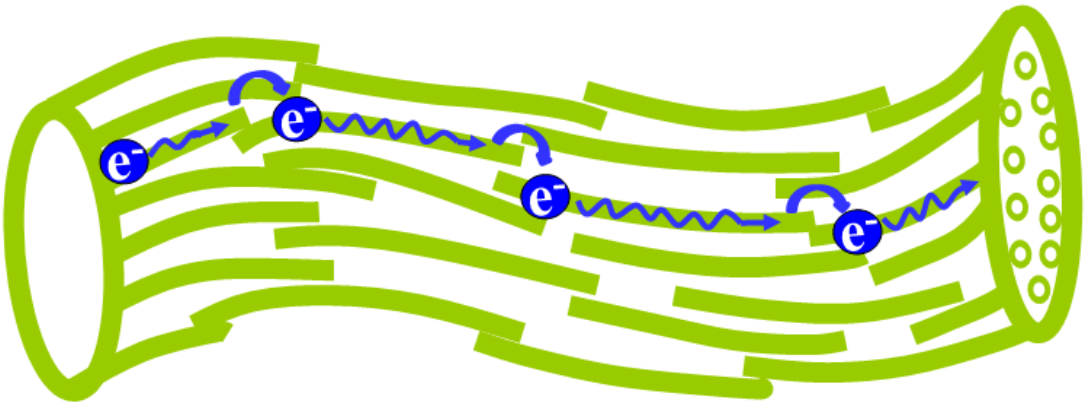

Figure S8. Schematic illustration of the electron transportation in local area of a CNT fiber.

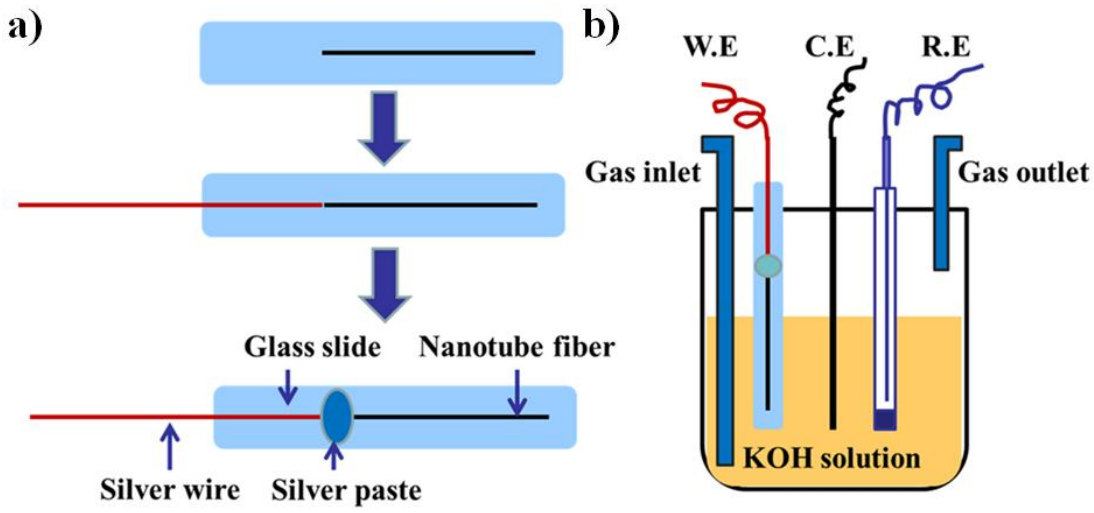

Figure S9. a) Schematic illustration for fabrication of a pure CNT or composite fiber as working electrode for electrochemical characterization; b) Schematic illustration for a three-electrode system using a pure CNT or composite fiber as working electrodes (W.E), platinum wire as counter electrode (C.E), and Ag/AgCl as reference electrode (R.E).

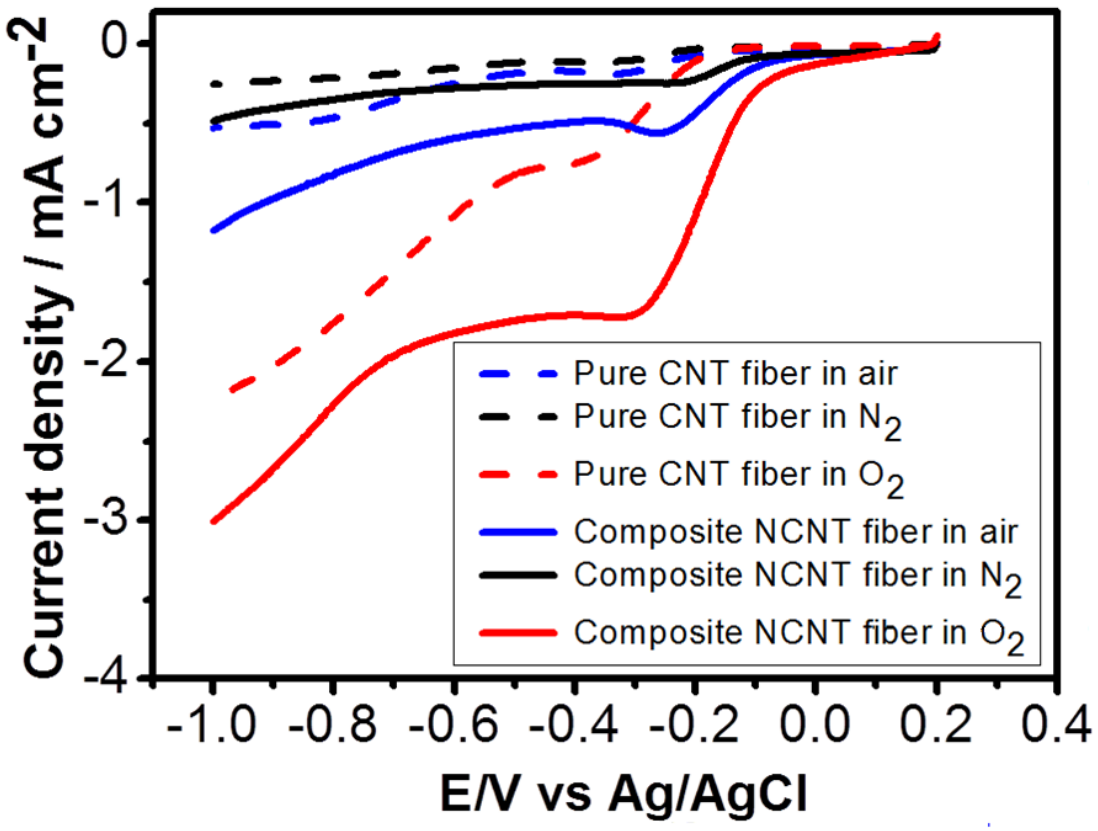

Figure S10. Linear sweep voltammograms for the dioxygen electroreduction in 0.1 M KOH based on pure CNT and composite NCNT fiber electrodes under different atmospheres with the same scan rate of 100 mV s^{-1}. The dashed lines correspond to linear sweep voltammograms for pure CNT fibers in air-saturated (black color), N_2-saturated (blue color), and O_2-saturated (red color) atmospheres, respectively. The solid lines correspond to linear sweep voltammograms for composite fiber in air-saturated (black color), N_2-saturated (blue color), and O_2-saturated (red color) atmospheres, respectively.

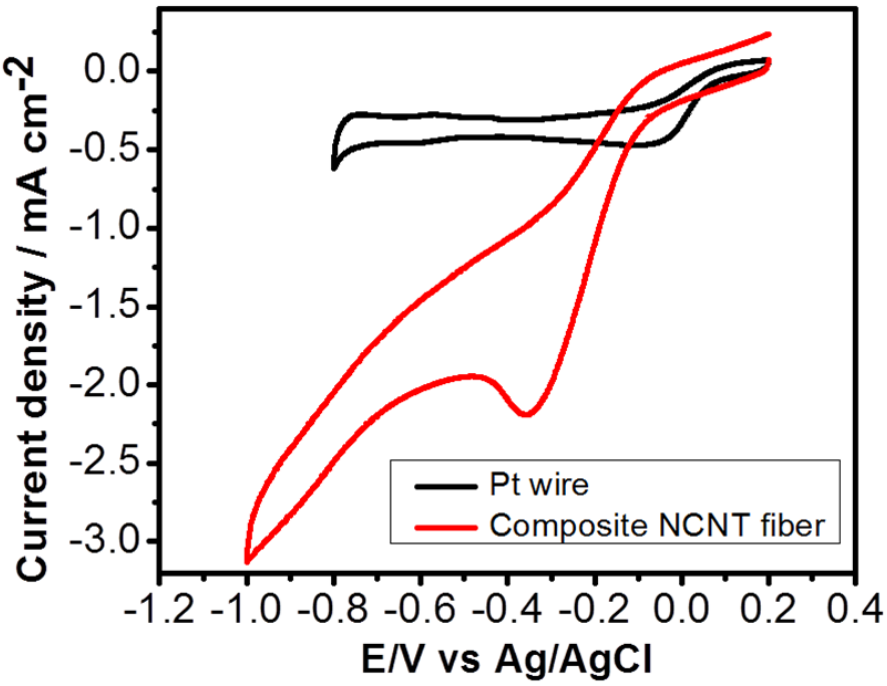

Figure S11. Cyclic voltammograms of the ORR for the composite NCNT fiber (red line) and platinum wire (black line) in 0.1 M O_2-saturated KOH aqueous solution with the same scan rate of 100 mV s^{-1}.

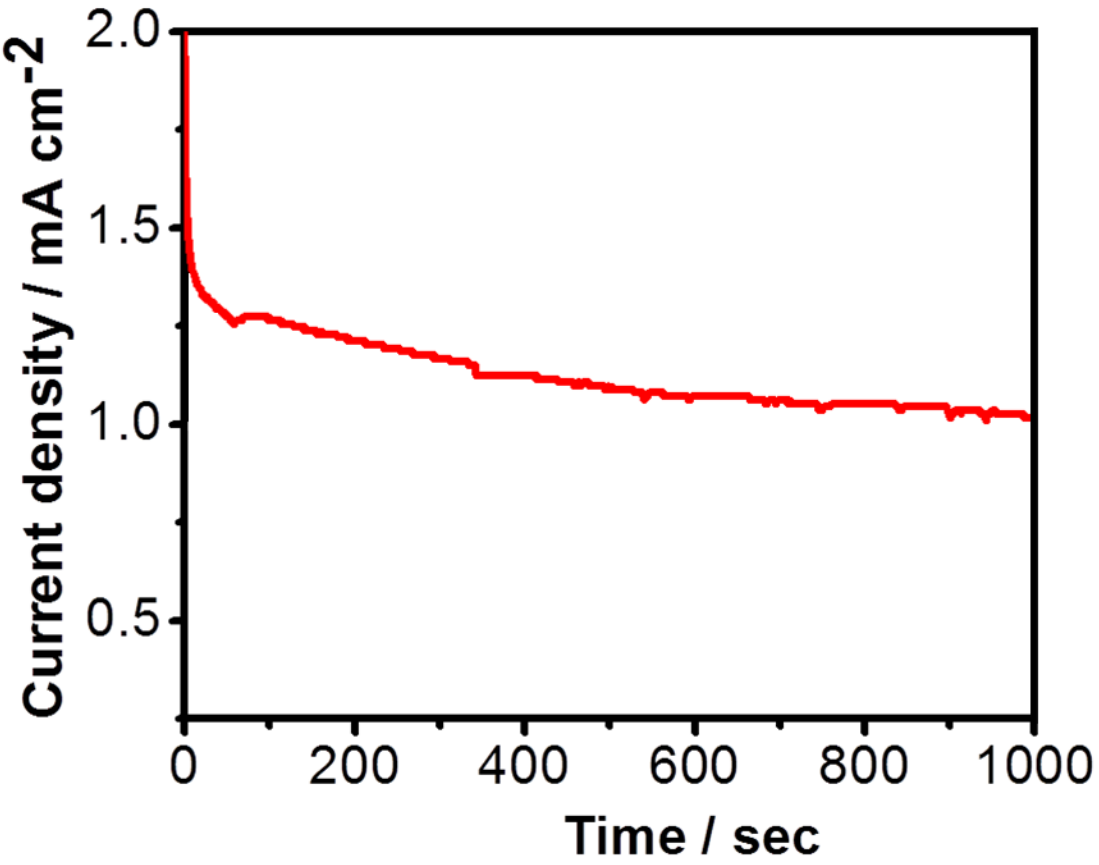

Figure S12. The i-t chronoamperometric responses of composite NCNT fiber at –0.25 V in 0.1 M O_2-saturated KOH solution in 1000 s.

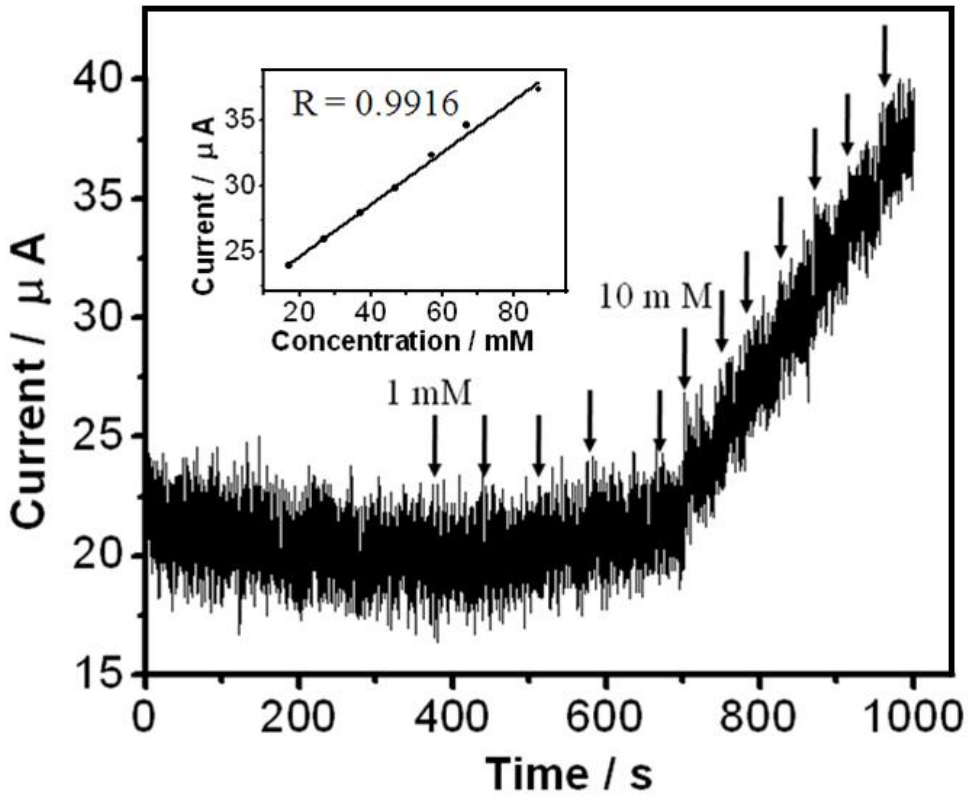

Figure S13. Current–time curve of CNT fiber electrode for successive addition of H_2O_2 (indicated by arrows with marked concentration) to 50 mM phosphate buffered saline solution (pH of 7.4) at +0.30 V vs Ag/AgCl. Inset: calibration curve shows the linear electrode response to H_2O_2 addition with correlation efficient of 0.9916.

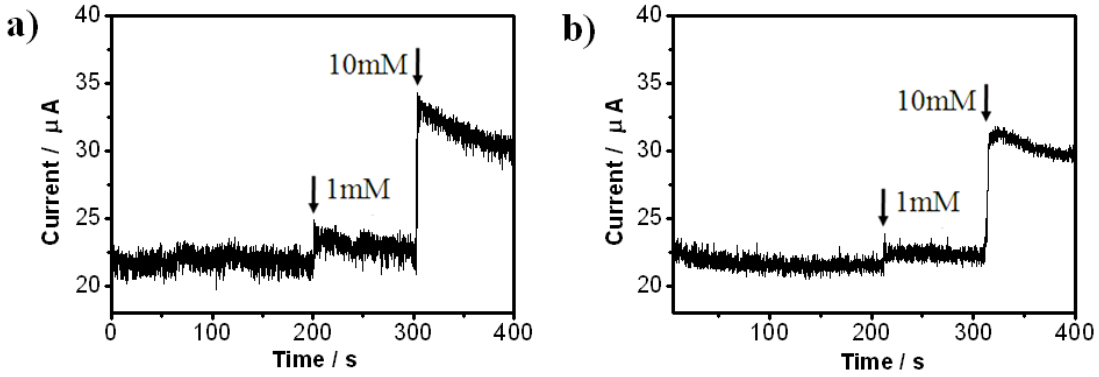

Figure S14. Current-time curves of a NCNT composite fiber in 50 mM phosphate buffered saline solution (pH of 7.4) after successive addition of 1 and 10 mM H_2O_2 at +0.3 V at the first (a) and fifth (b) cycles. One cycle was realized after alternate sensing and washing operations of NCNT composite fiber.

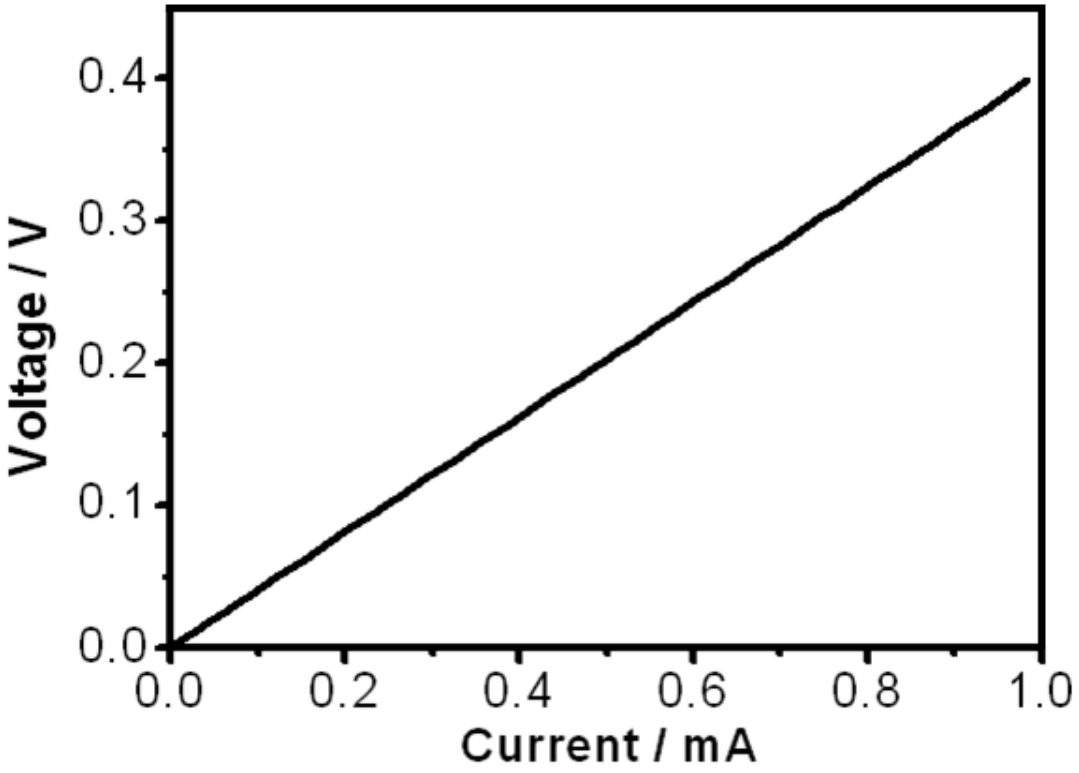

Figure S15. A typical I-V curve of a CNT fiber at room temperature. The fiber has a diameter of 10.5 μm and a length of 3.5 mm. The electrical conductivity is calculated as 400 S/cm.