Supporting information

Synthesis of Carbon Nanotubes@Mesoporous Carbon Core-Shell Structured Electrocatalysts via a Molecule-Mediated Interfacial Co-assembly Strategy

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Experimental Section

Synthesis of carbon nanotubes@non-mesoporous N-doped carbon (CNTs@NC) core-shell structured nanofibers: The preparation process was similar as that of the carbon nanotubes@mesoporous N-doped carbon (CNTs@mesoNC) core-shell structured nanofibers without adding TMB.

Synthesis of the mesoporous N-doped carbon spheres (mesoNCSs): The preparation process was similar as that of the CNTs@mesoNC core-shell structured nanofibers without adding carbon nanotubes.

Synthesis of the graphene oxide@mesostructured polydopamine (GO@mesoPDA) core-shell structured nanosheets: The GO was prepared from natural graphite powder using a modified Hummers method. [1] The preparation process of the GO@mesoPDA core-shell structured nanosheets was similar as that of the CNTs@mesoPDA core-shell structured nanofibers except that the obtained GO nanosheets were used as the cores.

Synthesis of CdS@mesostructured polydopamine (CdS@mesoPDA) core-shell structured nanospheres: The CdS nanospheres were synthesized as following the literature procedures. [2] The preparation process of the CdS@mesoPDA core-shell structured nanospheres was similar as that of the CNTs@mesoPDA core-shell structured nanofibers except that the obtained CdS nanospheres were used as the cores.

Synthesis of Fe_2O_3@mesostructured polydopamine (Fe_2O_3@mesoPDA) core-shell structured nanocubics: The Fe_2O_3 nanocubics were synthesized as following the literature procedures. [3] The preparation process of the Fe_2O_3@mesoPDA core-shell

structured nanocubics was similar as that of the CNTs@mesoPDA core-shell structured nanofibers except that the obtained Fe_2O_3 nanocubics were used as the cores.

Synthesis of resorcinol-formaldehyde@mesostructured polydopamine (RF@mesoPDA) core-shell structured nanospheres: The RF nanospheres were synthesized as following the literature procedures. [4] The preparation process of the RF@mesoPDA core-shell structured nanospheres was similar as that of the CNTs@mesoPDA core-shell structured nanofibers except that the obtained RF nanospheres were used as the cores.

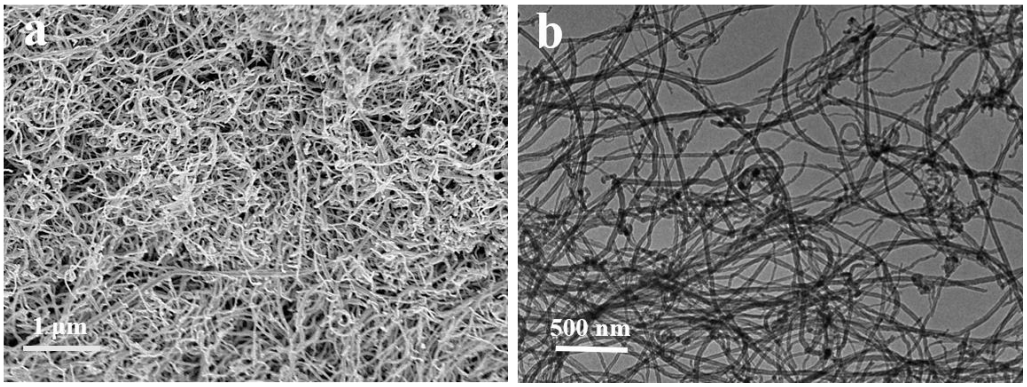

Figure S1. (a) SEM and (b) TEM images of the hydroxyl functionalized CNTs with a diameter of ~ 30 nm and length of several of micrometers.

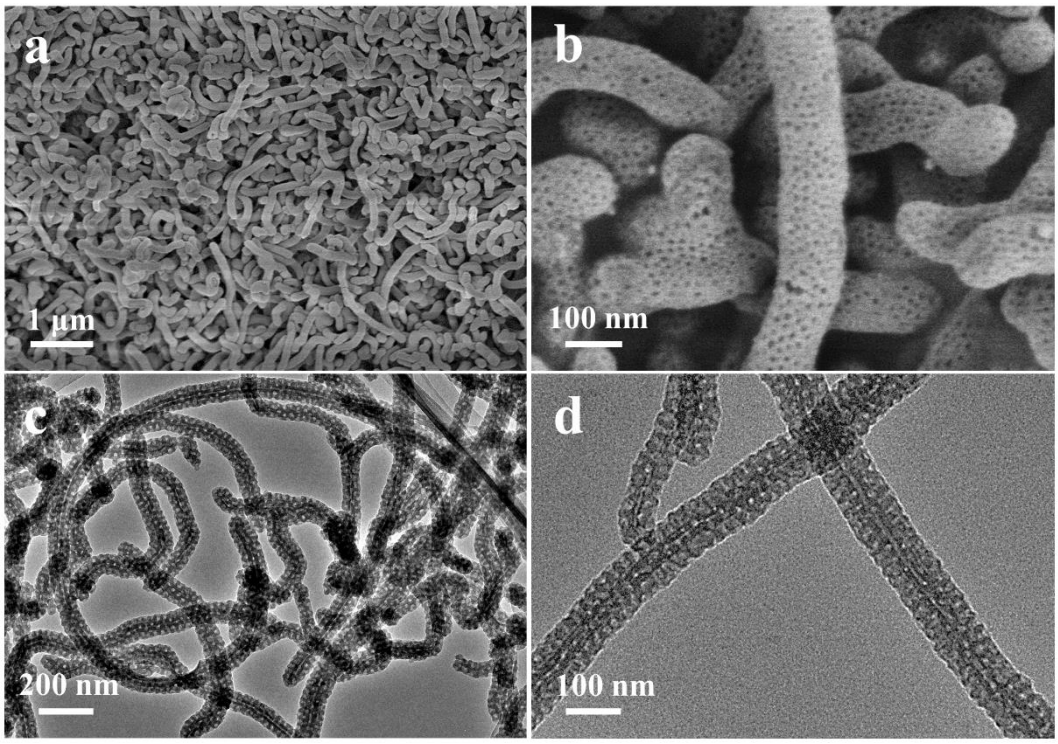

Figure S2. (a, b) SEM and (b, d) TEM images with different magnifications of the CNTs@mesoPDA core-shell structured nanofibers prepared *via* the co-assembly of F127-polydopamine composited micelles on carbon nanotubes with the mediation of TMB.

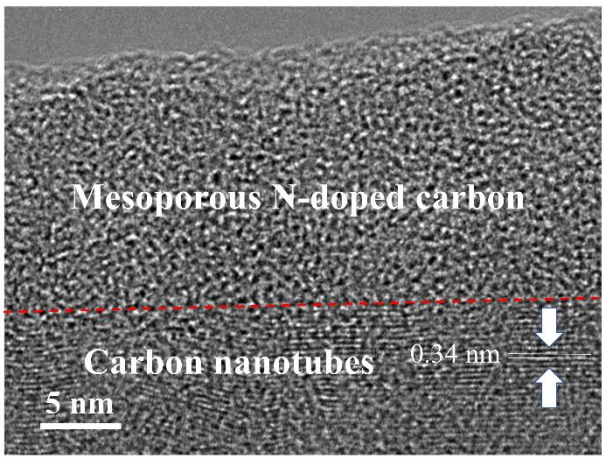

Figure S3. The high-resolution TEM (HRTEM) image of the CNTs@mesoNC core-shell structured nanofibers carbonized in a hypoxic atmosphere at 800 °C. There is a clear boundary between the crystallized carbon nanotube core and the amorphous mesoporous N-doped carbon shell, confirming the successful coating process.

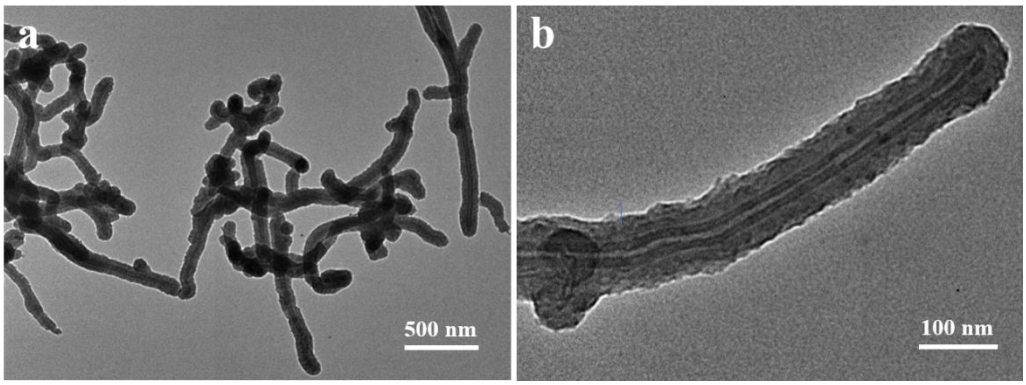

Figure S4. (a, b) TEM images of the CNTs@NC core-shell structured nanofibers with different magnifications. The sample was prepared by a similar process as that of the CNTs@mesoNC core-shell structured nanofibers without adding TMB.

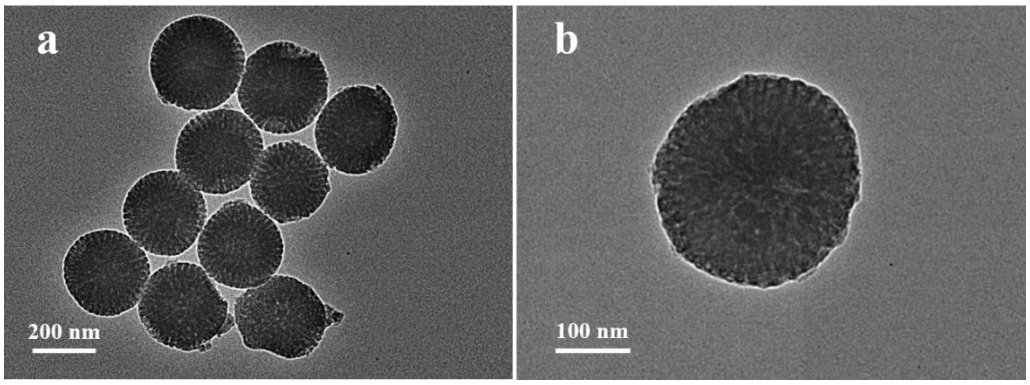

Figure S5. (a, b) TEM images of the mesoNCSs with different magnifications. The preparation process was similar as that of the CNTs@mesoNC core-shell structured nanofibers without adding CNTs.

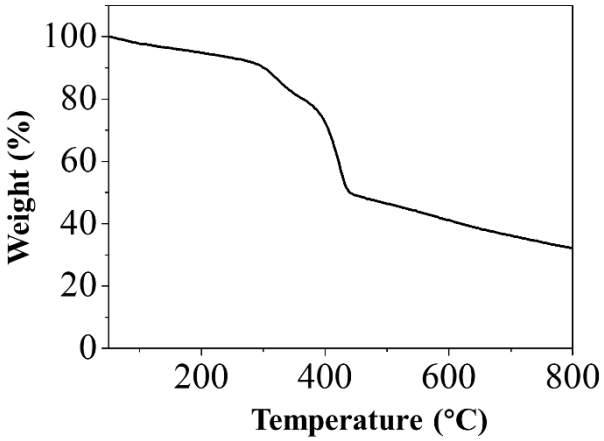

Figure S6. Thermogravimetric analysis (TGA) curve of the CNTs@mesoPDA under N_2 atmosphere with a ramp rate of 5 °C min^{-1}.

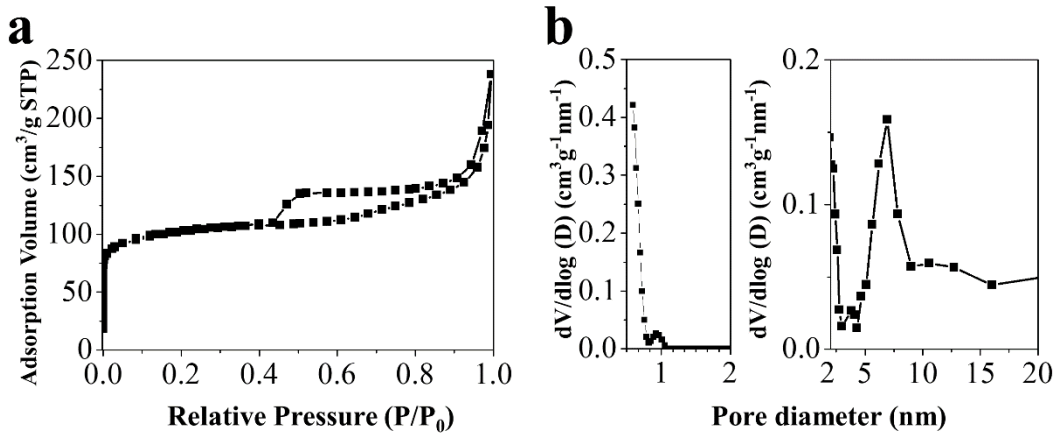

Figure S7. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution curves of the CNTs@mesoNC core-shell structured nanofibers carbonized in pure N_2 at 800 °C. The corresponding micropore size distribution curves were calculated by the NLDFT method and mesopore size distribution curves were calculated by the BJH method. The surface area was calculated to be 352 m^2 g^{-1}. Only a distinct pore size distribution centered at 7.3 nm is observed.

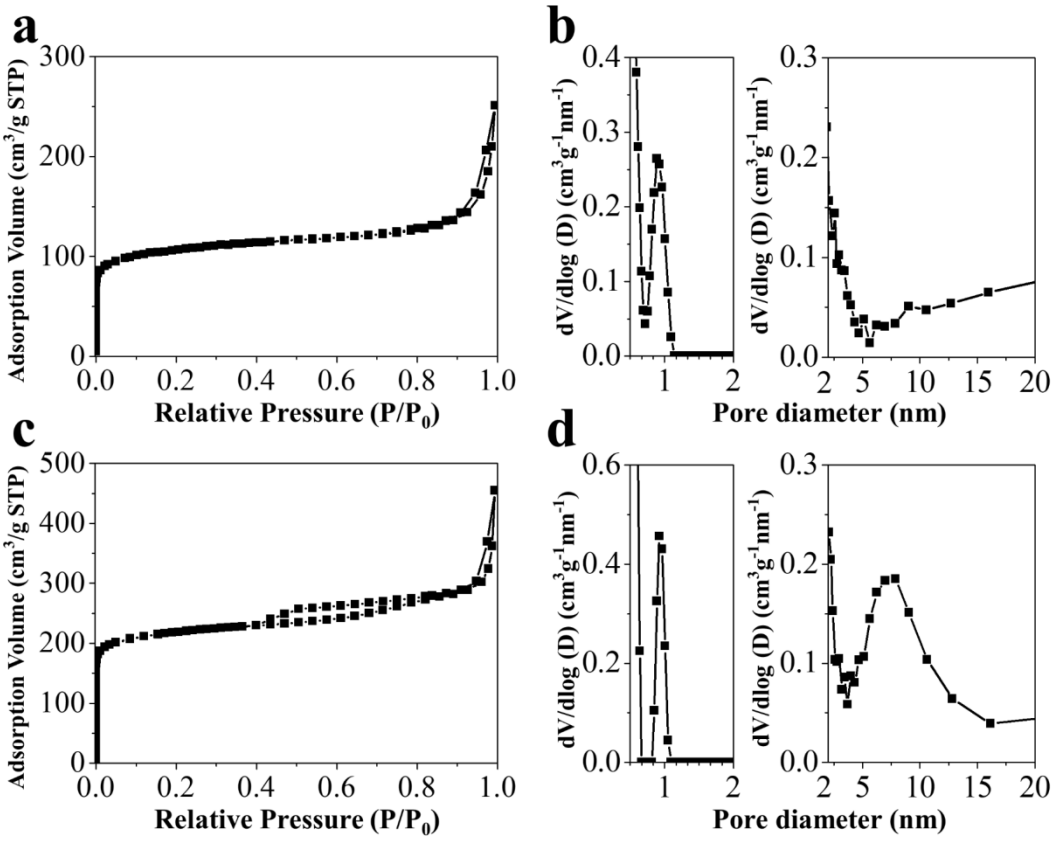

Figure S8. Nitrogen adsorption–desorption isotherms and pore size distribution curves of (a, b) the CNTs@NC core-shell structured nanofibers and (c, d) mesoNCSs. The corresponding micropore size distribution curves were calculated by the NLDFT method and mesopore size distribution curves were calculated by the BJH method. The surface area of the CNTs@NC core-shell structured nanofibers was calculated to be 367 m^2 g^{-1}. The CNTs@NC core-shell structured nanofibers show a distinct pore size distribution centered at 0.9 nm. The surface area of the mesoNCSs was calculated to be 752 m^2 g^{-1}. The mesoNCSs possess a micropore and mesopore centered around 1.0 and 7.8 nm.

Table S1. Texture parameters of the different samples.

Samples	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	V_{mi} (cm^3 g^{-1})	V_{me} (cm^3 g^{-1})	Pore size (nm)
CNTs@NC	367	0.37	0.14	0.23	0.9, -
mesoNCSs	752	0.70	0.26	0.44	1.0, 7.8
CNTs@mesoNC	768	0.57	0.27	0.30	0.9, 6.9
CNTs@mesoNC-N_2	352	0.37	0.10	0.27	-, 7.3

Notation: S_{BET}, BET surface area; V_t, total pore volume; V_{mi}, volume of micropores; V_{me}, volume of mesopores; CNTs@NC, carbon nanotubes@non-mesoporous N-doped carbon core-shell structured nanofibers carbonized in a hypoxic atmosphere at 800 °C; mesoNCSs, mesoporous N-doped carbon spheres carbonized in a hypoxic atmosphere at 800 °C; CNTs@mesoNC, carbon nanotubes@mesoporous N-doped carbon core-shell structured nanofibers carbonized in a hypoxic atmosphere at 800 °C; CNTs@mesoNC-N_2, carbon nanotubes@mesoporous N-doped carbon core-shell structured nanofibers carbonized in pure N_2 at 800 °C.

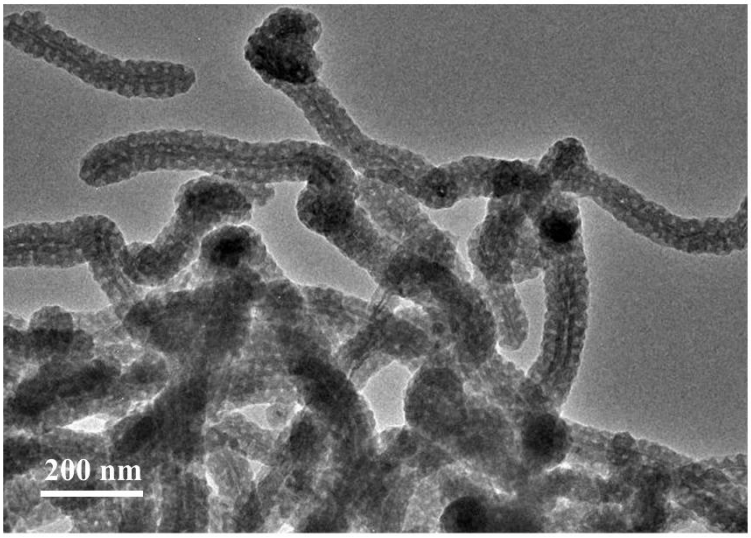

Figure S9. TEM image of the CNTs@mesoNC core-shell structured nanofibers prepared by using pristine CNTs without surface functionalizations as the cores.

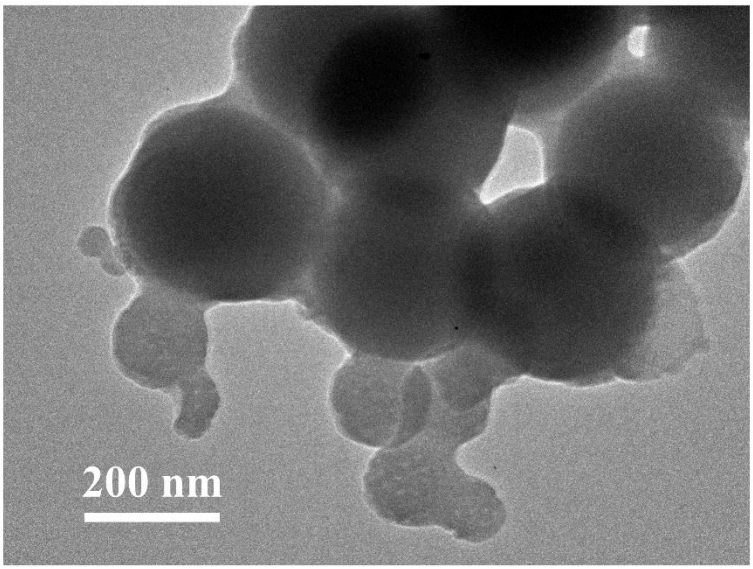

Figure S10. TEM image of the SiO_2/mesoPDA mixtures prepared by a similar process as that of the CNTs@mesoNC core-shell structured nanofibers except that the super-hydrophilic SiO_2 spheres were used as the cores.

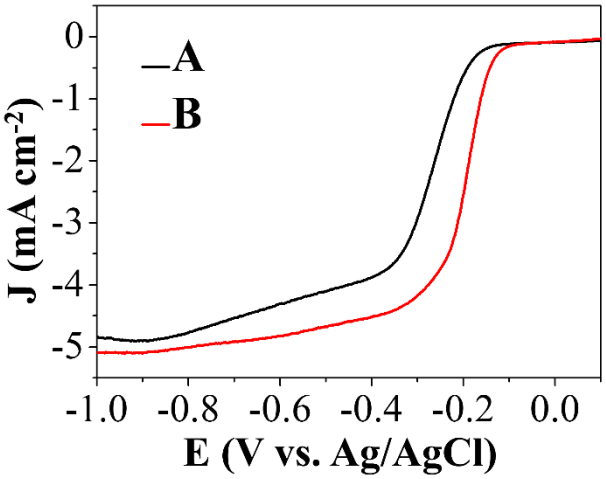

Figure S11. Linear sweep voltammetry (LSV) measurements of (a) the CNTs@mesoNC core-shell structured nanofibers carbonized in pure N_2 at 800 °C and (b) the CNTs@mesoNC core-shell structured nanofibers carbonized in a hypoxic atmosphere at 800 °C.

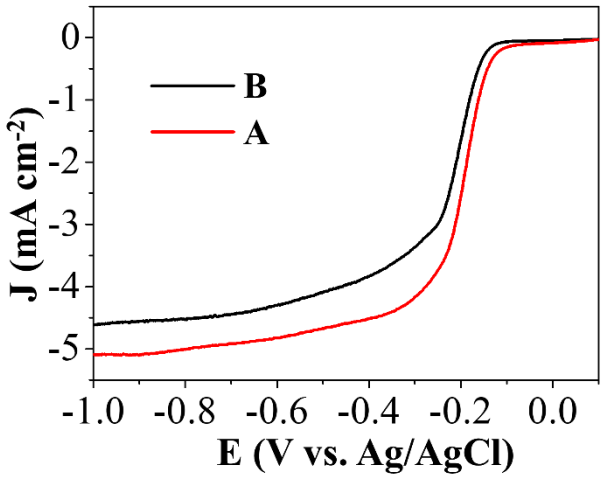

Figure S12. Linear sweep voltammetry (LSV) measurements of the CNTs@mesoNC core-shell structured nanofibers carbonized in a hypoxic atmosphere at (a) 800 and (b) 900 °C.

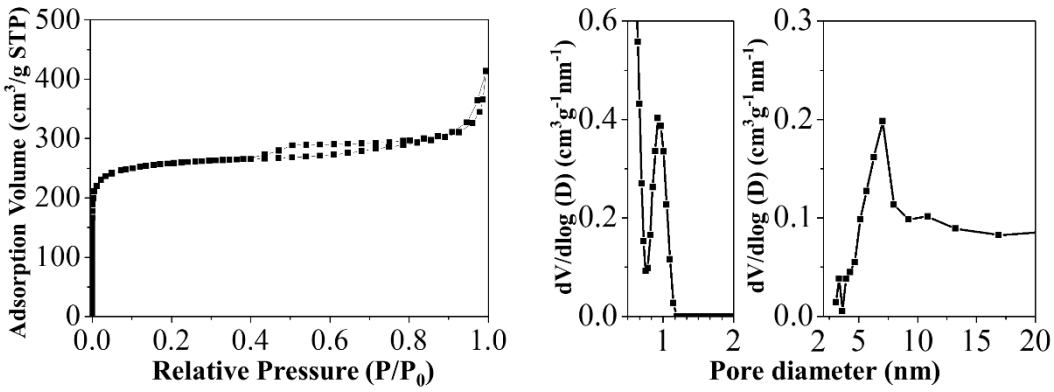

Figure S13. (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution curves of the CNTs@mesoNC core-shell structured nanofibers carbonized in a hypoxic atmosphere at 900 °C. The corresponding micropore size distribution curve was calculated by the NLDFT method and mesopore size distribution curve was calculated by the BJH method. The surface area was calculated to be 887 m^2 g^{-1}. These nanofibers possess a micropore and a mesopore centered around 0.9 and 7.0 nm.

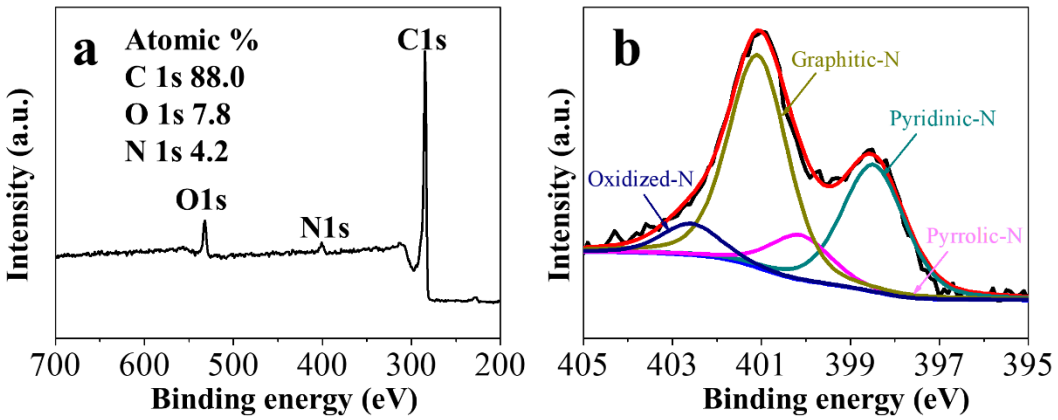

Figure S14. (a) XPS survey scan and (b) the corresponding high-resolution N1s spectrum of the CNTs@mesoNC core-shell structured nanofibers carbonized in a hypoxic atmosphere at 900 °C. The total nitrogen content was calculated to be 4.2 at%. The percentages of pyridinic, pyrrolic, graphitic and oxidized N groups are about 31.8, 11.1, 50.0 and 7.1 at%, respectively.

Table S2. Comparison on the ORR activity of various carbon-based electrocatalysts.

Electrocatalyst	Onset potential (V)	CV peak potential (V)	Limit current density (mA cm^{-2})	Reference
CNTs@mesoNC	0.92	0.77	5.09	This work
GO–PDA nanohybrids	0.90	0.71	3.50	5
Bowl-like mesoporous carbon particles	0.86	0.76	4.80	6
N-doped graphene	0.91	0.70	N/A	7
Nitrogen-doped multilayer graphene	0.84	N/A	4.60	8
walnut-shaped carbon particles	N/A	0.72	N/A	9
N-doped mesoporous carbon spheres	0.86	0.71	N/A	10

Notation: All potentials in this table refer to that of RHE. The rotation rate is 1600 rpm for all samples.

References

[1] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc*., 1958, *80*, 1339.

[2] G. F. Lin, J.W. Zheng, R. Xu, *J. Phys. Chem. C*, 2008, 112, 7363.

[3] X. Y. Yu, H. Hu, Y. W. Wang, H. Y. Chen, X. W. Lou, *Angew. Chem. Int. Ed*., 2015, 54, 7395.

[4] J. Liu, S. Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Y. Zhao, G. Q. Lu, *Angew. Chem. Int. Ed*., 2011, 50, 5947.

[5] K. G. Qu, Y. Zheng, S. Dai, S. Z. Qiao, *Nanoscale*, 2015, 7, 12598.

[6] B. Y. Guan, L. Yu, X. W. Lou, *J. Am. Chem. Soc*., 2016, 138, 11306.

[7] H. P. Cong, P. Wang, M. Gong, S. H. Yu, *Nano Energy*, 2014, 3, 55.

[8] T. Xing, Y. Zheng, L. H. Li, B. C. C. Cowie, D. Gunzelmann, S. Z. Qiao, S. M. Huang, Y. Chen, *ACS Nano*, 2014, 8, 6856.

[9] B. Y. Guan, S. L. Zhang, X. W. Lou, *Angew. Chem. Int. Ed*., 2018, 57, 6176.

[10] B. Bayatsarmadi, Y. Zheng, M. Jaroniec, S. Z. Qiao, *Chem. Asian J*., 2015, 10, 1546.