

## Supporting Information

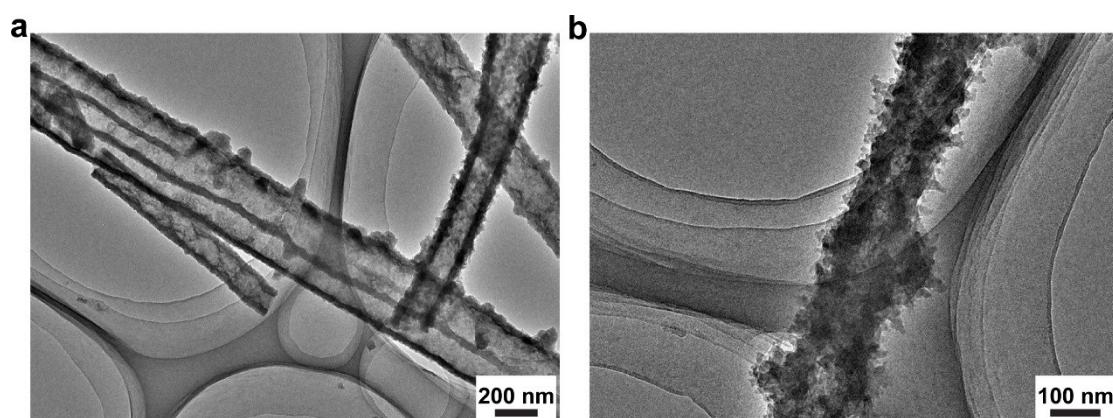
### Hierarchically Tubular Nitrogen-doped Carbon Structures for Oxygen Reduction Reaction

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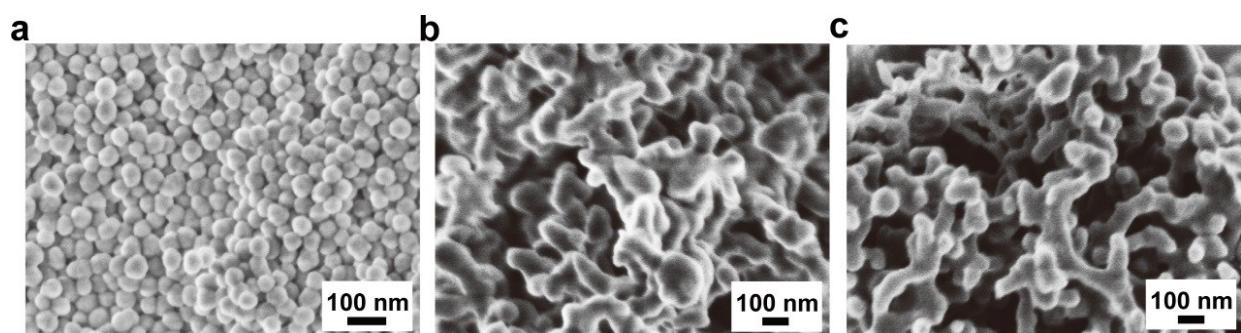
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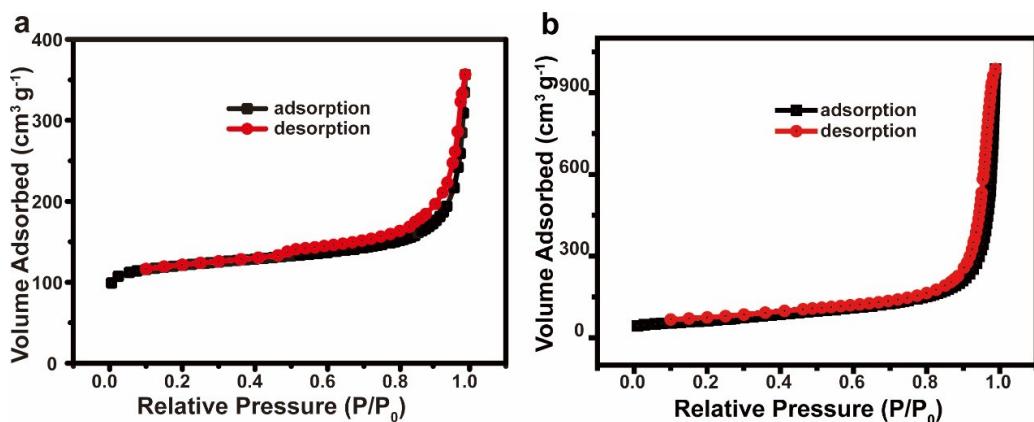
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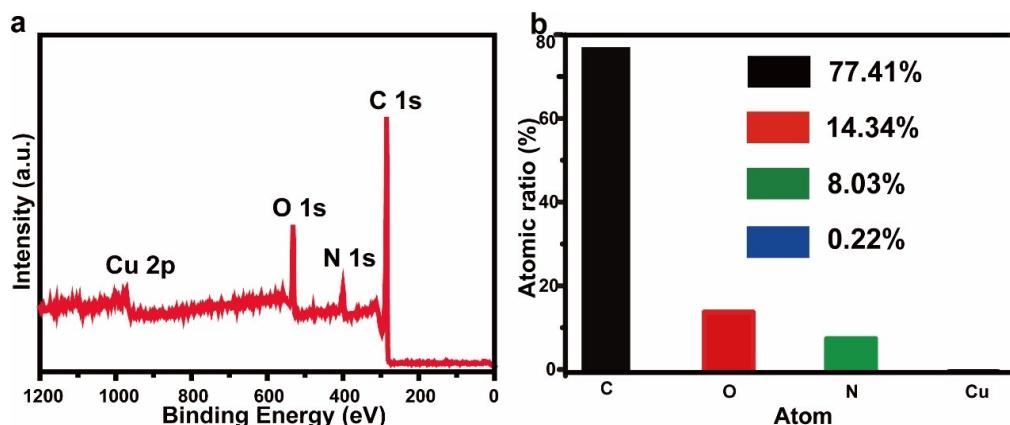
**Figure S1.** (a, b) TEM images of Cu<sub>2</sub>O-HT-NCTs.



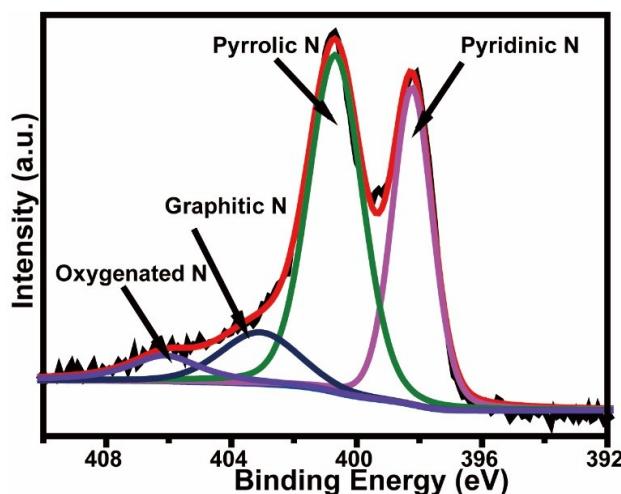
**Figure S2.** SEM images of (a) SiO<sub>2</sub> nanospheres, (b) SiO<sub>2</sub>-CNs and (c) Si-CNs.



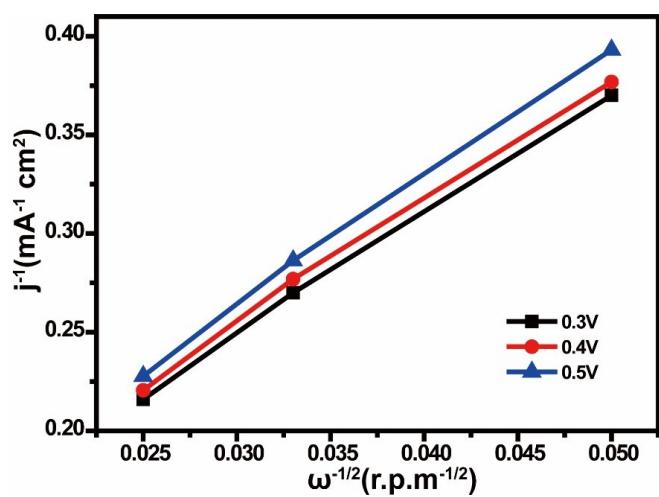
**Figure S3.** N<sub>2</sub> adsorption-desorption curves of (a) the HT-NCTs and (b) Si-CNs.



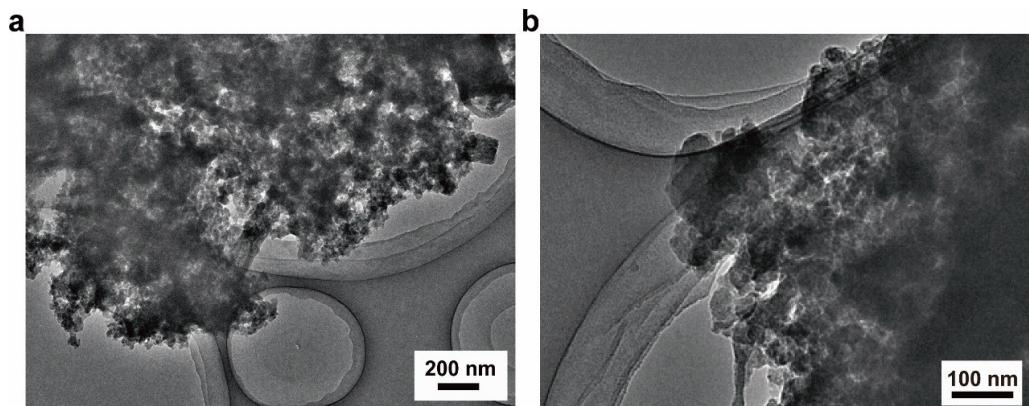
**Figure S4.** (a) XPS spectrum of HT-NCTs. (b) Different atomic proportion of HT-NCTs.



**Figure S5.** High-resolution XPS spectra of N 1s in Si-CNs.



**Figure S6.** K–L plots of HT-NCTs at the potential of 0.3, 0.4 and 0.5 V.



**Figure S7.** (a, b) TEM images of HT-NCTs after stability tests.

**Table S1. Proportions of Different Kinds of Nitrogen in HT-NCTs**

	Pyridinic N	Pyrrolic N	Graphitic N	Oxygenated N	Total
Relative	<b>26.72%</b>	<b>15.23%</b>	<b>42.64%</b>	<b>15.41%</b>	<b>100%</b>
content					
Total	<b>2.34 at%</b>	<b>1.33 at%</b>	<b>3.73 at%</b>	<b>1.35 at%</b>	<b>8.03 at%</b>
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**Table S2. Proportions of Different Kinds of Nitrogen in Si-CNPs**

	Pyridinic N	Pyrrolic N	Graphitic N	Oxygenated N	Total
Relative	<b>34.27%</b>	<b>48.77%</b>	<b>10.79%</b>	<b>6.17%</b>	<b>100%</b>
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Total	<b>1.81 at%</b>	<b>2.57 at%</b>	<b>0.57 at%</b>	<b>0.33 at%</b>	<b>5.28 at%</b>
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**Table S3. Comparison of Different ORR Catalysts**

Reference	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	Limiting current (mA cm <sup>-2</sup> )	Loading (mg cm <sup>-2</sup> )
S1	<b>0.9</b>	<b>0.76</b>	<b>5.79</b>	<b>0.204</b>
S2	<b>0.9</b>	<b>0.79</b>	<b>4.1</b>	<b>0.102</b>
S3	<b>0.86</b>	<b>0.77</b>	<b>4.8</b>	<b>0.498</b>
S4	<b>0.83</b>	<b>0.72</b>	<b>4.5</b>	<b>0.396</b>
S5	<b>0.88</b>	<b>0.76</b>	<b>3.3</b>	<b>0.251</b>
<b>This work</b>	<b>0.89</b>	<b>0.76</b>	<b>4.9</b>	<b>0.137</b>

**References:**

- S1. H. Yu, L. Shang, T. Bian, R. Shi, G. I. N. Waterhouse, Y. Zhao, C. Zhou, L.-Z. Wu, C.-H. Tung and T. Zhang, *Adv. Mater.*, 2016, **28**, 5080-5086.
- S2. X. Fu, X. Hu, Z. Yan, K. Lei, F. Li, F. Cheng and J. Chen, *Chem. Commun.*, 2016, **52**, 1725-1728.
- S3. C. Hu, Y. Zhou, R. Ma, Q. Liu and J. Wang, *J. Power Sources*, 2017, **345**, 120-130.
- S4. G. Panomsuwan, N. Saito, T. Ishizaki, *ACS Appl. Mater. Interfaces*, 2016, **8**, 6962-6971.
- S5. A. Mulyadi, Z. Zhang, M. Dutzer, W. Liu and Y. Deng, *Nano Energy*, 2017, **32**, 336-346.