Electronic Supplementary Information

Flexible 3D Porous CuO Nanowire Arrays for Enzymeless Glucose Sensing: *In Situ* Engineered versus *Ex Situ* Piled

Jianfei Huang, Yihua Zhu*, Xiaoling Yang, Wei Chen, Ying Zhou, and Chunzhong Li*

Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

*Address correspondence to: yhzhu@ecust.edu.cn (Y. Zhu); czli@ecust.edu.cn (C. Li).

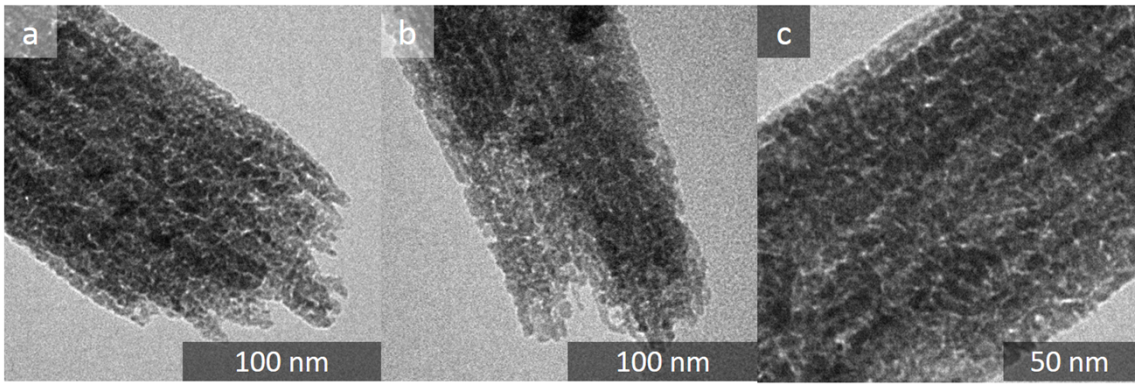

Fig. S1 TEM images of porous CuO nanowires.

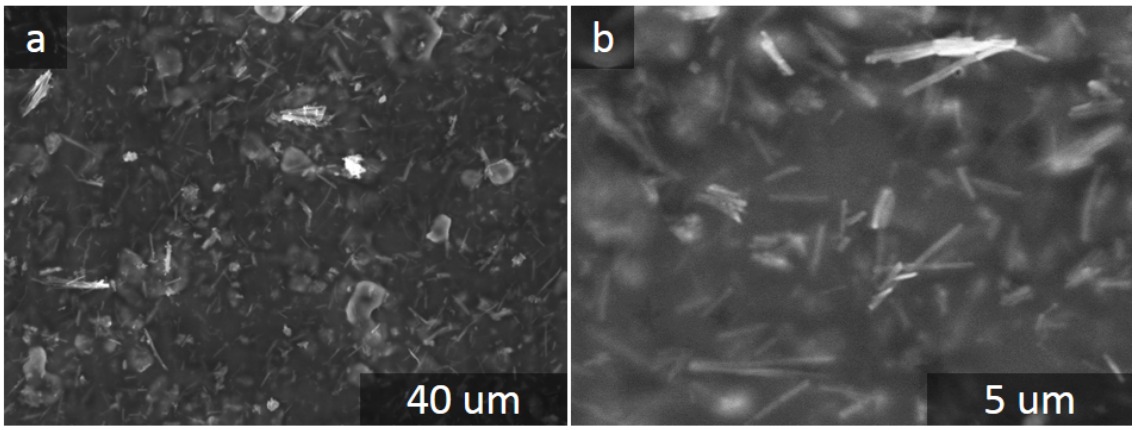

Fig. S2 SEM images of the composite film of CuO NWs entrapped in the Nafion binder at (a) low and (b) high magnifications.

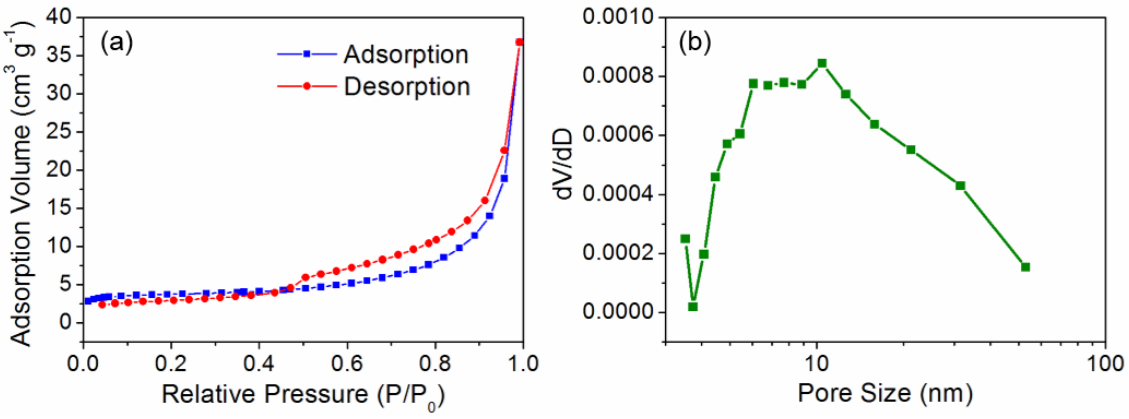

Fig. S3 (a) N_2 sorption isotherms and (b) pore size distribution of the CuO NWs.

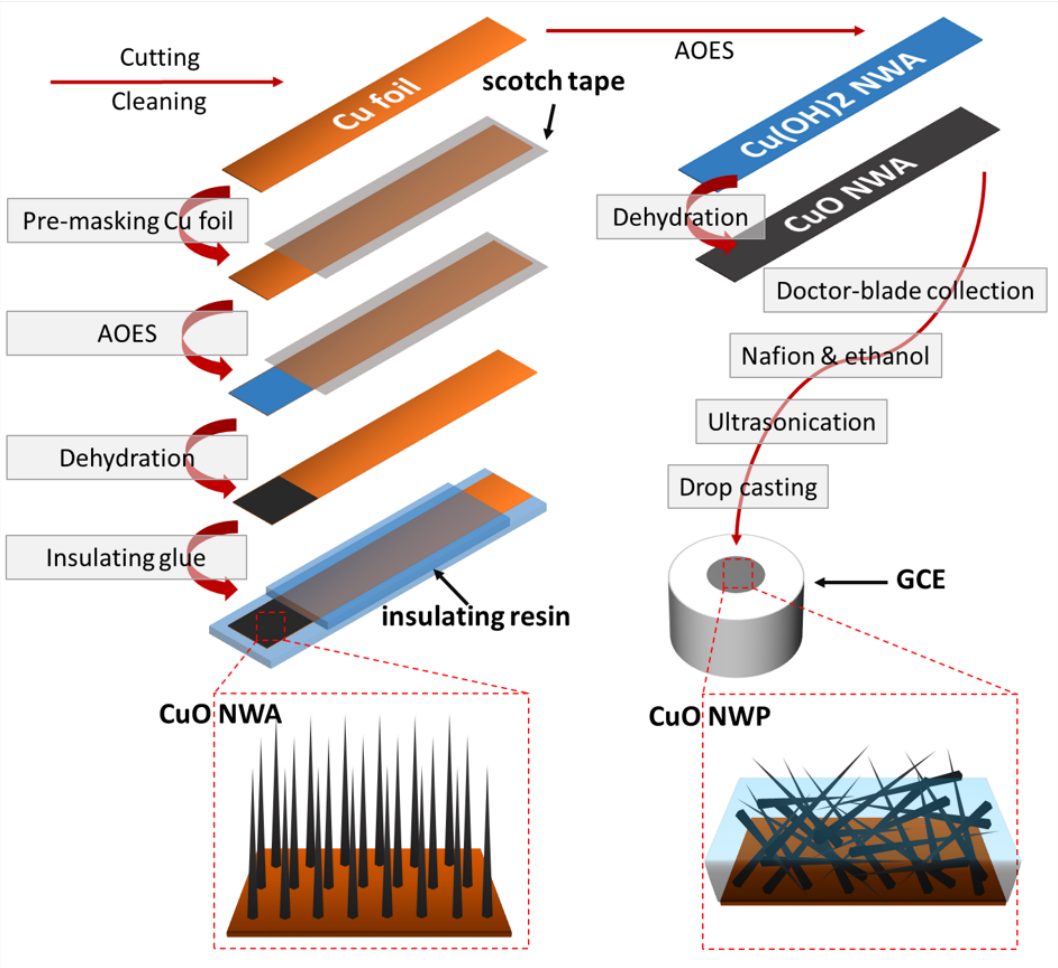

Fig. S4 Schematic illustrations of electrodes fabrication procedures.

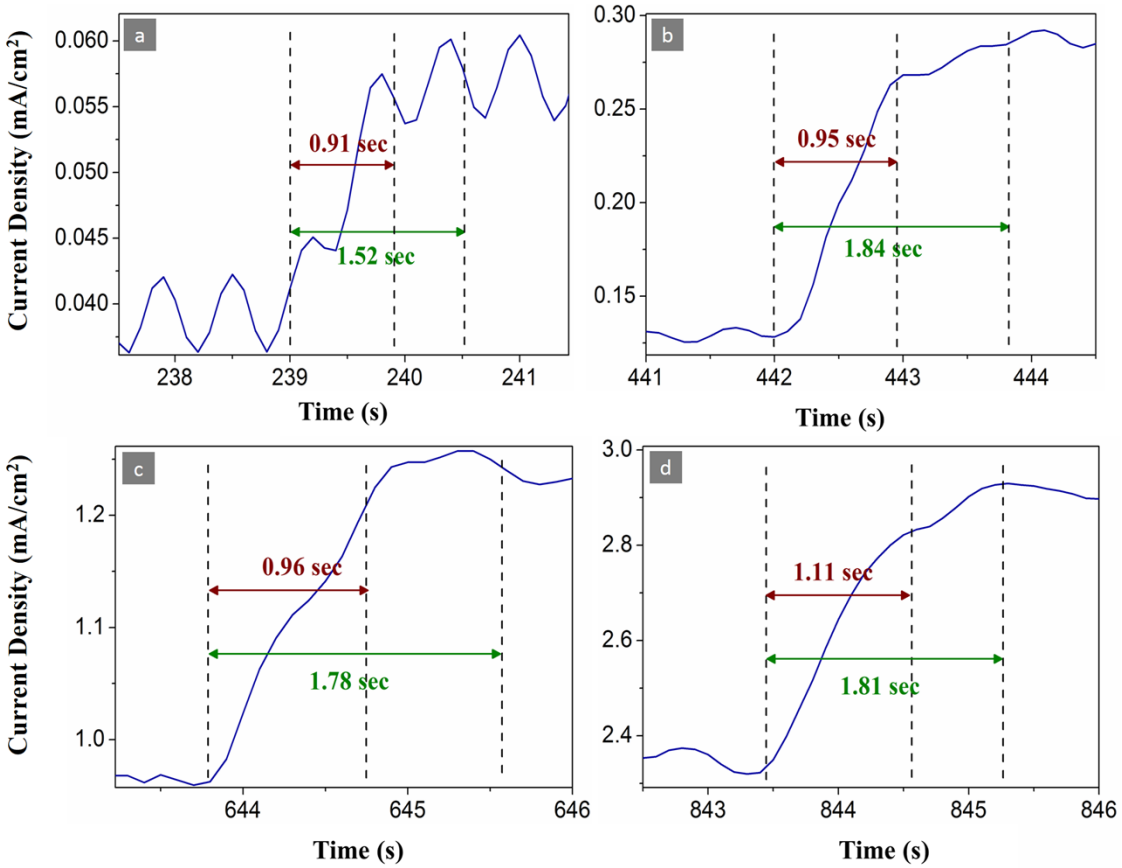

Fig. S5 Current response time to addition of the glucose of various concentrations: (a) 10 uM, (b) 100 uM, (c) 200 uM and (d) 500 uM. Double-headed arrows indicate time required for 90% current change (red) and reaching plateau (green), respectively.

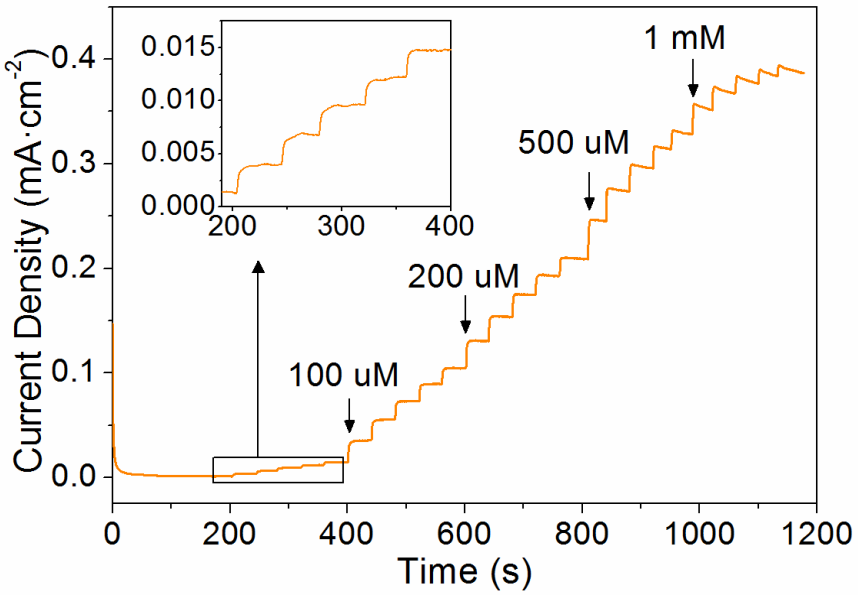

Fig. S6 Amperometric *i*-t test with successive addition of glucose for the NWP under +0.35 V. Inset shows the magnified current curve with stepwise addition of 10 uM analyte.

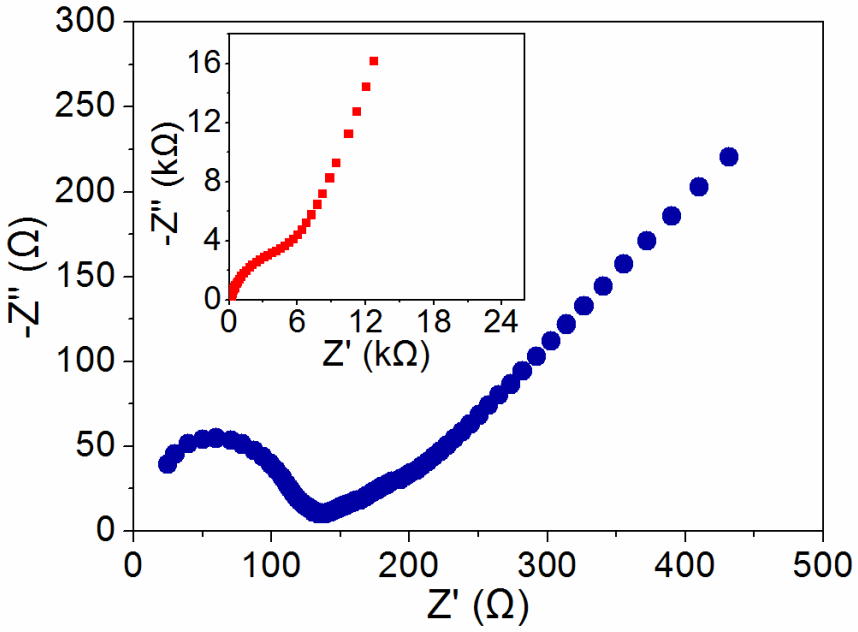

Fig. S7 Nyquist plot of the NWA, the inset is the Nyquist plot of the NWP.

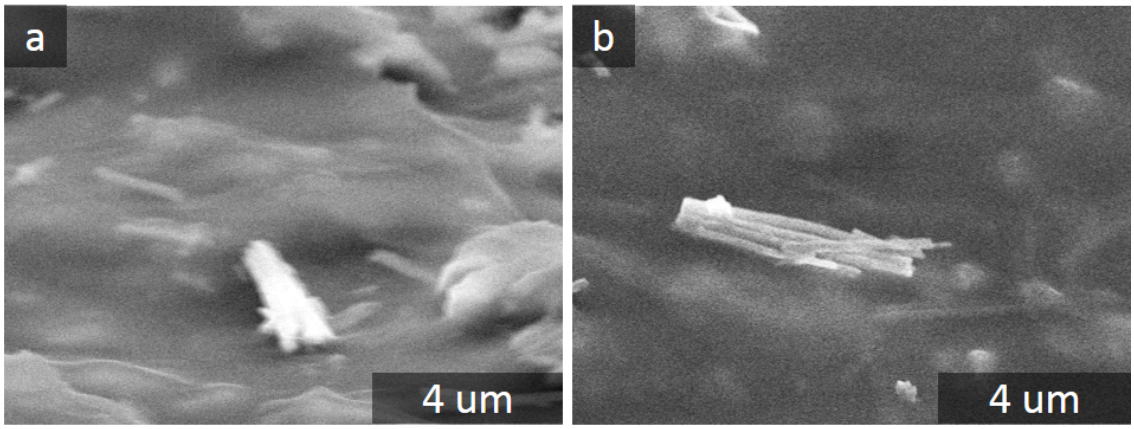

Fig. S8 SEM images of fractured parts of CuO nanowires at the NWP-Nafion film.

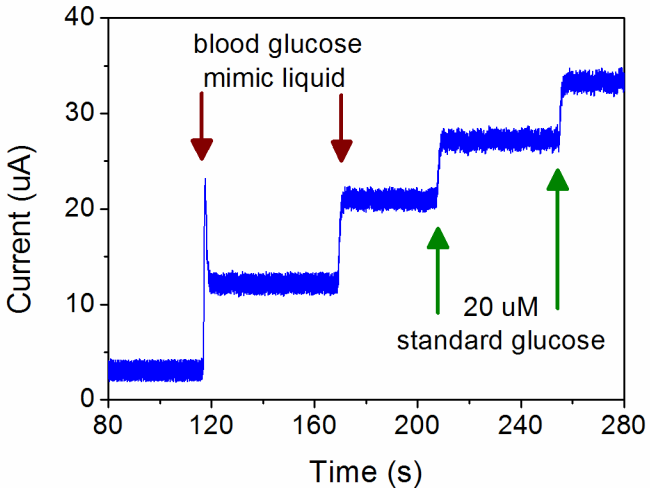

Fig. S9 Recovery test with injection of commercial mimic solution of blood glucose and 20 uM standard of glucose. The concentration of blood glucose mimic solution is calculated to be 24 uM per injection.

Table S1. Parameter comparison of enzymeless sensors for glucose

Sensor Electrode	Sensitivity ($uA \cdot mM \cdot cm^{-2}$)	Response Time (s)	Linear Range (mM)	Detection Limit (uM)	Ref.
CuO NWs/GCE	648.2	<5	-	2	1
CuO-Cu NWs/GCE	121.5	<5	0.1-12	50	2
CuO NWs/Cu	2450	<1	0.0004-2	0.049	3
CuO NF[a]/GCE	431.3	~1	0.006-2.5	0.8	4
CuO NF/ITO	873	<1	0.0002-1.3	0.04	5
CuO NB[b]/Cu	582	~2	-	<1	6
CuO NR[c]/Graphite	371.43	<10	0.004-8	4	7
CuO Hollow Polyhedron/GCE	1112	~2	up to 4	0.33	8
CuO NS[d]/GCE	404.53	-	up to 2.55	1	9
CuO NP[e]/GO/GCE	262.52		0.00279-2.03	0.69	10
CuO NC[f]/Graphene/GCE	1360	<5	0.002-4	0.7	11
CuO-SWCNT[g]/ITO	1610	1-2	0.05-1.8	0.05	12
Co_3O_4 NF/GCE	36.25	<7	up to 2.04	0.97	13
Ni NW/Cu	4243	-	0.003-2	0.1	14
Pt Nf[h]/MWCNT[i]/graphene	11.06	~12	1-7	387	15
$Ni(OH)_2$/3DGF[j]	2650	<5	0.001-1.17	0.34	16
Au@Pd NPs-ionic liquids/GCE	1870	-	0.000005-0.005	0.001	17
Cu@C NWs/GCE	437.8	<5	up to 3	0.05	18
Pd-Ni/Si NW	190.72	<8	0-20	2.88	19
Co_2N_x/N-doped GO[k]	1167	<5	0.01-4.75	6.93	20
CuO NWA/Cu	1420.3	1-2	up to 2.55	5.1	this work
CuO NWP/GCE	250.1	1-2	up to 2.05	1.9	this work

Abbreviations of Table S1:

[a] Nanofiber, [b] Nanobelt, [c] Nanorod, [d] Nanosphere, [e] Nanoparticle, [f] Nanocube, [g] Single-walled Carbon Nanotube, [h] Nanoflower, [i] Multi-walled Carbon Nanotube, [j] Three-dimensional Graphene Foam, [k] Graphene Oxide

Table S2. Results of the recovery test for CuO NWA electrode

Found Concentraion of Mimic Liquid (uM)	Added Standard Concentration (uM)	Found Concentraion of After Addition (uM)	Recovery (%)	Relative Deviation (%)
24	0	23.53	—	1.96
48	0	50.81	—	5.85
48	20	70.38	97.85	—
48	40	88.88	95.18	—

Calculation:

Relative Deviation herein stands for the deviation of found glucose concentration of the mimic liquid (C_{found}) from the known concentration of the spiked sample (C_{Known}), and is calculated with the formula as below.

$$\text{Relative Deviation} = 100\% \times (C_{found} - C_{Known}) / C_{Known}$$

Recovery herein stands for the value corresponding to adding standard recovery with non-standard sample in presence and is calculated with the formula as below.

$$\text{Recovery} = 100\% \times (C_{AA} - C_{found}) / C_{AS}$$

Where C_{AA} and C_{AS} stand for concentration found after adding standard sample and added concentration of standard sample, respectively.

REFERENCES

1 Y. Zhang, Y. Liu, L. Su, Z. Zhang, D. Huo, C. Hou and Y. Lei, *Sens. Actuators, B*, 2014, **191**, 86.

2 G. Wang, Y. Wei, W. Zhang, X. Zhang, B. Fang and Z. L. Wang, *Microchim. Acta*, 2010, **168**, 87.

3 Z. Zhuang, X. Su, H. Yuan, Q. Sun, D. Xiao and M. M. F. Choi, *Analyst*, 2008, **133**, 126.

4 W. Wang, L. Zhang, S. Tong, X. Li and W. Song, *Biosens. Bioelectron*., 2009, **25**, 708.

5 G. Liu, B. Zheng, Y. Jiang, Y. Cai, J. Du, H. Yuan and D. Xiao, *Talanta*, 2012, **101**, 24.

6 T, Soejima, H. Yagyu, N. Kimizuka and S. Ito, *RSC Adv*., 2011, **1**, 187.

7 X. Wang, C. Hu, H. Liu, G. Du, X. He and Y. Xi, *Sens. Actuators, B* **2010**, *144*, 220.

8 C. Kong, L. Tang, X. Zhang, S. Sun, S. Yang, X. Song and Z. Yang, *J. Mater. Chem. A*, 2014, **2**, 7306.

9 E. Reitz, W. Jia, M. Gentile, Y. Wang and Y. Lei, *Electroanalysis* 2008, **20**, 2482.

10 J. Song, L. Xu, C. Zhou, R. Xing, Q. Dai, D. Liu and H. Song, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12928.

11 L. Luo, L. Zhu and Z. Wang, *Bioelectrochemistry*, 2013, **88**, 156.

12 N. Quoc Dung, D. Patil, H. Jung and D. Kim, *Biosens. Bioelectron*., 2013, **42**, 280.

13 Y. Ding, Y. Wang, L. Su, M. Bellagamba, H. Zhang and Y. Lei, *Biosens. Bioelectron*., 2010, **26**, 542.

14 R. K. Shervedani, M. Karevan and A. Amini, *Sens. Actuators, B*, 2014, **204**, 783.

15 S. Badhulika, R. K. Paul, T. Terse, A. Mulchandani, *Electroanalysis*, 2014, **26**, 103.

16 X. Dong, X. Wang, J. Wang, H. Song, X. Li, L. Wang, P. Chen, W. Huang and X. Dong, *Nanoscale*, 2014, **6**, 7424.

17 X. Chen, H. Pan, H. Liu and M. Du, *Electrochim. Acta*, 2010, **56**, 636.

18 Y. Zhao, Z. He and Z. Yan, *Analyst*, 2013, **138**, 559.

19 S. Hui, J. Zhang, X. Chen, H. Xu, D. Ma, Y. Liu and B. Tao, *Sens. Actuators, B*, 2011, **155**, 592.

20 L. Kong, Z. Ren, S. Du, J. Wu and H. Fu, *Chem. Commun.*, 2014, **50**, 4921.