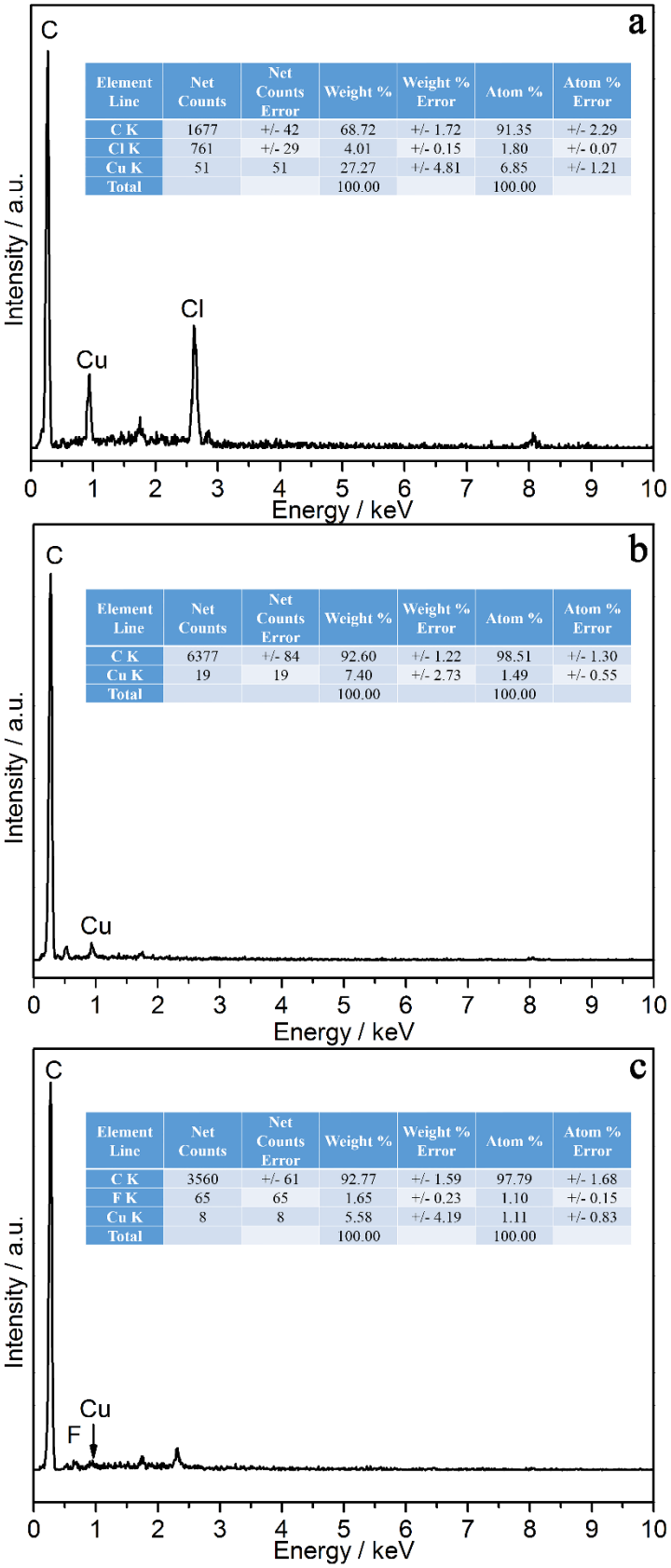
Electronic Supplementary Material (ESI) for RSC Advances.

Hierarchical PS/PANI supported Cu(II) nanocatalysts: Facile synthesis and study of its catalytic application in aerobic oxidation

Jie Yu [a], Yi Luan [a], Yue Qi [a], Junying Hou [a], Wenjun Dong [b], Mu Yang [a], Ge Wang [a]

[a]. *School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P. R. China Fax: +86 10 62327878; Tel: +86 10 62333765; E-mail: gewang@mater.ustb.edu.cn*

[b]. *Center for Optoelectronics Materials and Devices, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China*



Element Line	Net Counts	Net Counts Error	Weight %	Weight % Error	Atom %	Atom % Error
C K	1677	+/- 42	68.72	+/- 1.72	91.35	+/- 2.29
Cl K	761	+/- 29	4.01	+/- 0.15	1.80	+/- 0.07
Cu K	51	51	27.27	+/- 4.81	6.85	+/- 1.21
Total			100.00		100.00	

Element Line	Net Counts	Net Counts Error	Weight %	Weight % Error	Atom %	Atom % Error
C K	6377	+/- 84	92.60	+/- 1.22	98.51	+/- 1.30
Cu K	19	19	7.40	+/- 2.73	1.49	+/- 0.55
Total			100.00		100.00	

Element Line	Net Counts	Net Counts Error	Weight %	Weight % Error	Atom %	Atom % Error
C K	3560	+/- 61	92.77	+/- 1.59	97.79	+/- 1.68
F K	65	65	1.65	+/- 0.23	1.10	+/- 0.15
Cu K	8	8	5.58	+/- 4.19	1.11	+/- 0.83
Total			100.00		100.00	

Figure S1 EDX spectrum of the supported Cu catalysts: a) PS/PANI@$CuCl_2$, b) PS/PANI@$Cu(NO_3)_2$ and c) PS/PANI@$Cu(CF_3SO_3)_2$.

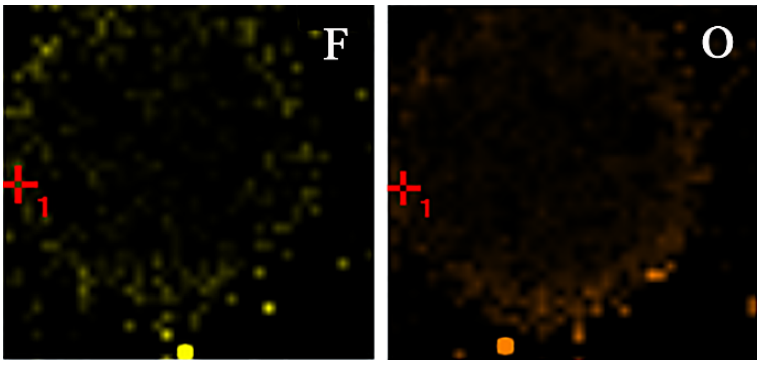
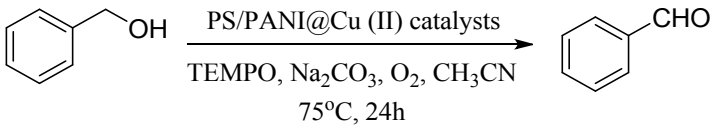


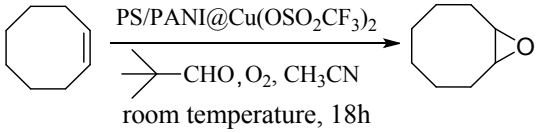
Figure S2. EDX elemental maps of F and O in PS/PANI@Cu(CF_3SO_3)$_2$ catalyst.

General procedure for aerobic oxidation of benzyl alcohol using supported Cu (II) catalysts



Benzyl alcohol (1 mmol) and supported Cu (II) catalyst (based on 1 mol% Cu, 0.01 mmol, 12.1 mg of PS/PANI@$CuCl_2$ in Table 1 Entry 3, 35.4 mg of PS/PANI@$Cu(NO_3)_2$ in Table 1 Entry 4 and 41.1 mg of PS/PANI@$Cu(OSO_2CF_3)_2$ in Table 1 Entry 5) were added to acetonitrile (5 mL) with TEMPO (0.5 equiv.) and Na_2CO_3 (1 equiv.) in a 25 mL round-bottom flask. The reaction mixture was purged three times with oxygen stirred at 75 °C under 1 atm of O_2. After 24h, the solution was cooled to room temperature and the PS/PANI supported Cu (II) catalysts were filtered from the solution by centrifugation. The filtered liquid samples were analyzed by GC-MS with nitrobenzene as an internal standard.

General procedure for aerobic epoxidation of cis-cyclooctene using PS/PANI@$Cu(OSO_2CF_3)_2$ catalyst



Cis-cyclooctene (1 mmol) and PS/PANI@$Cu(OSO_2CF_3)_2$ catalyst (based on 0.2 mol% Cu, 0.002 mmol, 8.2 mg of PS/PANI@$Cu(OSO_2CF_3)_2$ in Table 3) were added to acetonitrile (5 mL) with trimethylacetaldehyde (2 equiv.) in a 25 mL round-bottom flask. The reaction mixture was purged three times with oxygen stirred at room temperature under 1 atm of O_2. After the reaction, the PS/PANI@$Cu(OSO_2CF_3)_2$ catalysts were filtered from the solution by centrifugation. The filtered liquid samples were analyzed by GC-MS with nitrobenzene as an internal standard.

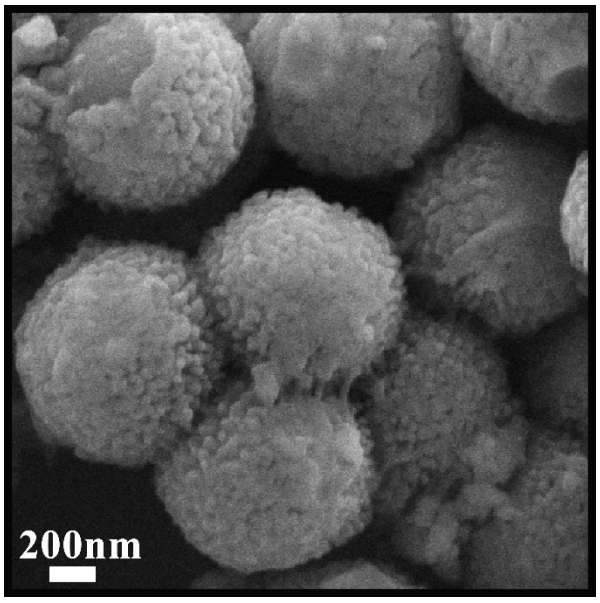


Figure S3 SEM images of PS/PANI@Cu(OSO2CF3)2 catalyst afte six recycles.

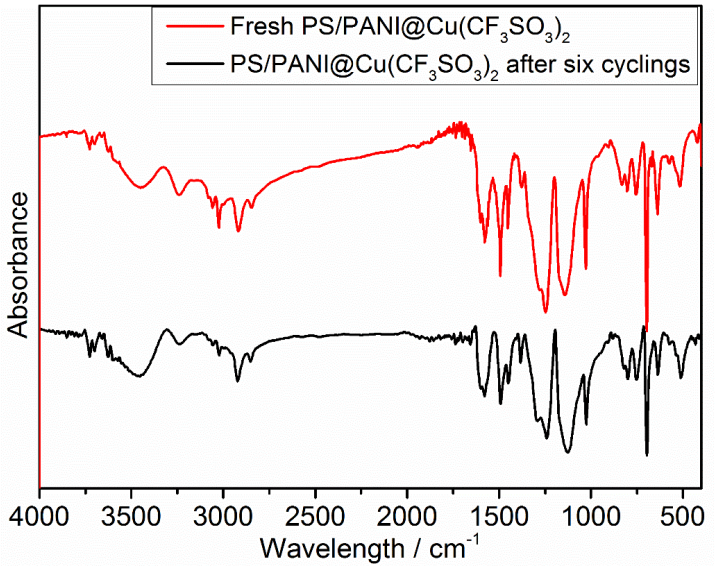


Figure S4 FTIR spectra of PS/PANI@Cu$(CF_3SO_3)_2$ (red, top) and PS/PANI@Cu$(CF_3SO_3)_2$ after six cyclings(black, bottom).

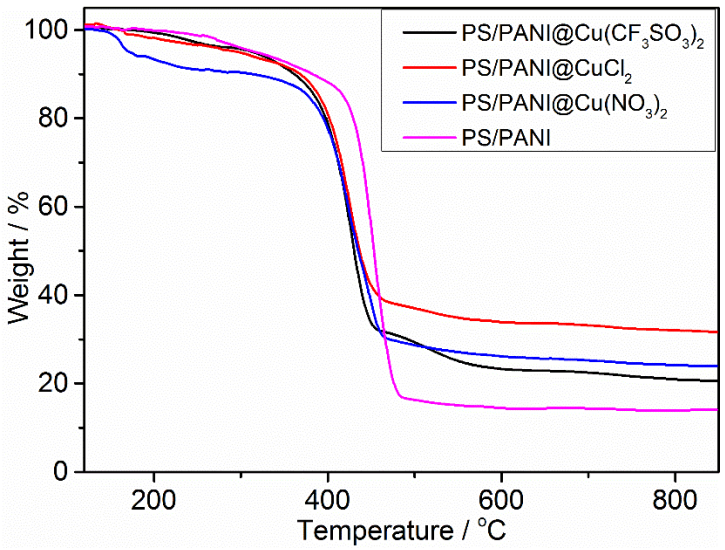


Figure S5. TG spectra of PS/PANI (Pink), PS/PANI@$CuCl_2$ (Red), PS/PANI@$Cu(NO_3)_2$ (Blue) and PS/PANI@$Cu(CF_3SO_3)_2$ (Black).