Electronic Supplementary Information

N-doped carbon nanofibers derived from bacterial cellulose as an excellent metal-free catalyst for selective oxidation of arylalkanes

Runkun Huang,[ab] Changyan Cao,[*ab] Jian Liu,[ab] Dongping Sun[c] and Weiguo Song[*ab]

[a.] Beijing National Laboratory for Molecular Sciences, Laboratory of Molecular Nanostructures and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China.

E-mail: cycao@iccas.ac.cn; wsong@iccas.ac.cn.

[b.] University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

[c.] Institute of Chemicobiology and Functional Materials, Nanjing University of Science and Technology, Nanjing, 210094, P. R. China.

1. Experimental section

1.1 Materials

Purified bacterial cellulose (BC) pellicles were provided by Dr. Dongping Sun (Nanjing University of Science and Technology). Urea (A.R.) was purchased from Beijing Chemical Reagent Company. Ethylbenzene (99%), anisole (99%), 4-ethylanisole (98+%), cumene (99%), diphenylmethane (99+%), fluorene (98+%) and tert-butyl hydroperoxide (70% aqueous solution) were provided by Alfa-Aesar. 2-Ethylnaphthalene (99%) and 1-ethyl-4-nitrobenzene (99%+) was purchased from TCI. Bibenzyl (99%) was produced by J&K scientific Co., Ltd. All the chemicals were obtained commercially (except 1-phenylethyl-tert-butyl-peroxide) and used as received without further purification.

Preparation of 1-phenylethyl-tert-butyl-peroxide. The target product was prepared according to previous literature (*J. Chem. Soc., Chem. Commun.*, 1994, **0**, 1823-1824). In a typical procedure, ethylbenzene (5 mmol), pyridine (3mL), acetic acid (0.3 ml), $Fe(NO_3)_3 \cdot 9H_2O$ (0.5 mmol) and TBHP (1 mmol) were added into 15mL pressure tube, then the pressure tube was sealed with a Teflon lid and heated at 70°C for 36h. After the reaction was completed, the reaction mixture was cooled to room temperature. The mixture was diluted by ethyl acetate, washed with water and evaporated under reduced pressure. The resulting residue was purified by column chromatography (silica gel, dichloromethane /n-hexane, 1:10) to obtain the desired product. The target product was determined by ^{1}H NMR and MS-ESI.

^{1}H NMR (400MHz, CDCl3): δ 1.14 (9H, s, CH3), δ 1.40 (3H, d, CH3), δ 4.92 (1H, q, CH), δ 7.15-7.30 (5H, m, Ph); MS-ESI: Figure S10.

1.2 Catalyst preparation

Preparation of N-CNF. The BC pellicles were first cut into some squares, then frozen in liquid nitrogen (-196 °C), subsequently freeze-dried in a vacuum freeze dryer (Biocool Corporation, China) at a sublimating temperature of -53 °C and a pressure of 0.03mbar. Afterwards 1g urea was

put into a crucible first, and then 200mg obtained freeze-dried BC was placed above urea and separated by a quartz plate with holes to avoid the direct contact of urea and BC. The crucible containing precursors was covered by a crucible lid. Finally, BC enclosed in crucible were pyrolyzed with assistance of urea at 900 ºC in a horizontal tube furnace for 2 h with a heating rate of 3 ºC /min under flowing argon atmosphere. After cooling down to room temperature, the obtained samples were denoted as N-CNF.

Preparation of N-CNF without urea and N-CNF-NH$_3$. The samples N-CNF without urea and N-CNF-NH$_3$ were synthesized through the same procedure as N-CNF at 900 ºC for 2 h under a flowing of Ar and NH$_3$ atmosphere respectively without urea.

Preparation of N-rGO. The sample N-rGO was prepared through the same procedures as N-CNF except replacing BC with GO.

Preparation of N-CNF-mix. The sample N-CNF-mix was synthesized through the following procedures: BC pellicles were cut into some squares, and then the squares were immersed into urea aqueous solution with a certain concentration to make sure the weight ratio of BC to urea is 5. Afterwards, BC-urea mixture were freeze dried in a vacuum freeze dryer. Finally, the obtained BC-urea mixture were pyrolyzed at 900 ºC for 2 h with a heating rate of 3 ºC /min under flowing argon atmosphere.

1.3 Catalyst characterization

The morphology and microstructures of the samples were characterized by scanning electron microscopy (JEOL, JSM-6701F) and high-resolution transmission electron microscopy (JEOL, JEM-2100F). EDS mappings of the materials were conducted using a scanning TEM (STEM) equipped with an EDS detector (JEOL 2100F). X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 200 mA. XPS measurement was performed on a VG Scientific ESCALab220i-XL spectrometer using Al Kα radiation. The surface area of the products was measured by the Brunauer–Emmett–Teller (BET) method using N$_2$ adsorption and desorption isotherms on Micromeritics ASAP 2460 Surface Area and Porosity Analyzer at 77 K.

1.4 Catalytic activity test

Selective oxidation of arylalkanes test. Substrate (0.5 mmol), catalyst (5.0 mg), TBHP (500 μL, 70 wt% in water), and water (3 mL) were added into a 15 mL glass reaction tube sealed with a Teflon lid. The reaction mixture was stirred in a preheated 80 ºC oil bath for 12 h. After the reaction system cooled down to room temperature, 77 μL anisole was added to the system as the internal standard. 10 mL CH$_2$Cl$_2$ was added to extract organic compounds in the reaction system. For ethylbenzene, the organic phase was filtered, then analyzed by a GC (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and an Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). For toluene, the conversion was analyzed by a GC mentioned above and the selectivity was determined by a HPLC (Shimadzu LC-15C) equipped with a SPD-15C UV/vis detector, a CTO-15C column oven and the WondaSil C18 column (4.6 × 150 mm, particle size 5 μm). In recycle experiments, the reaction time was 12 h, and the catalyst was separated by centrifugation and washed with ethanol three times and dried under vacuum at 60℃ for 6h. The recovered catalyst was reused in the next run.

1.5 Reaction mechanism study

Detection of intermediates. Ethylbenzene (0.5 mmol), catalyst (5.0 mg), TBHP (500 μL, 70 wt% in water), and water (3 mL) were added into a 15 mL glass reaction tube sealed with a Teflon lid. The reaction mixture was stirred in a preheated 80 ℃ oil bath for 4.5h. After the reaction system suddenly cooled down by liquid nitrogen, 77 μL anisole was added to the system as the internal standard. 10 mL CH_2Cl_2 was added to extract organic compounds in the reaction system. The organic phase was filtered, then analyzed by a GC-MS (Shimadzu GCMS-QP2010 Ultra) equipped with a DB-5MS capillary column (0.25 mm in diameter, 30 m in length).

Detection of radicals. Ethylbenzene (0.5 mmol), catalyst (5.0 mg), TBHP (500 μL, 70 wt% in water), and water (3 mL) were added into a 15 mL glass reaction tube sealed with a Teflon lid. The reaction mixture was stirred in a preheated 80 ℃ oil bath for 3h. Then 100μL DMPO was added into the reaction system to capture radicals. After that, 3mL CH_3CN was added into reaction system to fully mix water and organic compounds. The mixture was finally cooled down by liquid nitrogen and filtered in 1 minute before doing electron paramagnetic resonance (EPR) test.

2. Supporting Figures and Tables
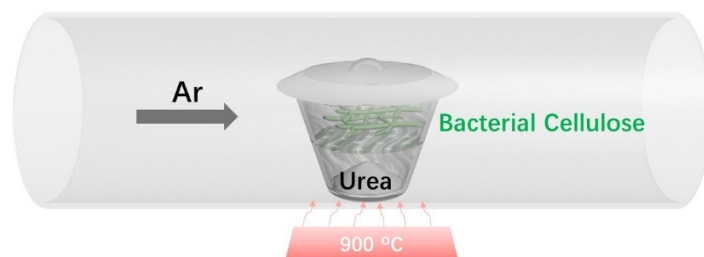
Scheme S1. Schematic illustration of preparation process of N-CNF.
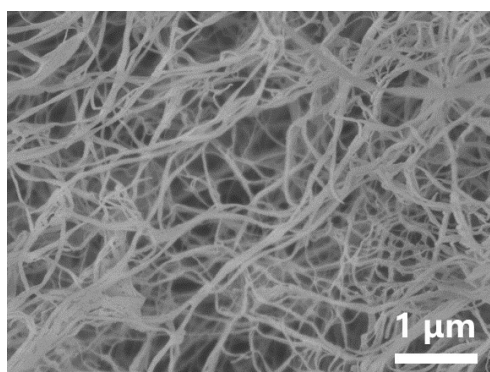
Figure S1. SEM image of freeze-dried BC.
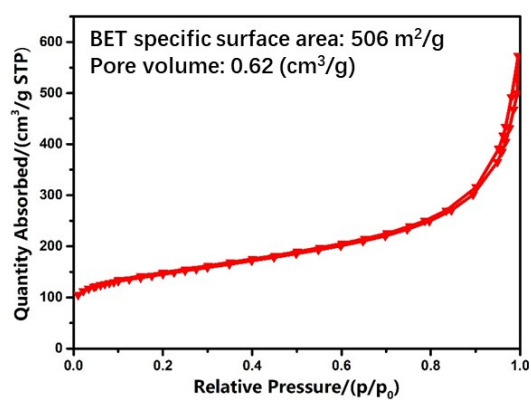
Figure S2. N_2 adsorption–desorption isotherms of N-CNF.
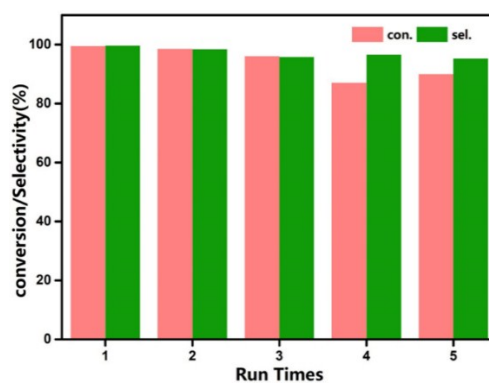
Figure S3. Reusability of N-CNF in selective oxidation of ethylbenzene.
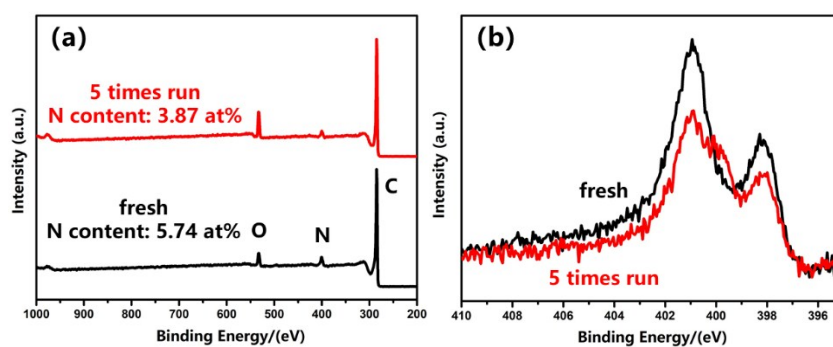
Figure S4. (a) Full XPS spectra of fresh N-CNF and recycled catalyst after 5 times run, (b) high resolution XPS of N1s of fresh N-CNF and recycled catalyst after 5 times run.
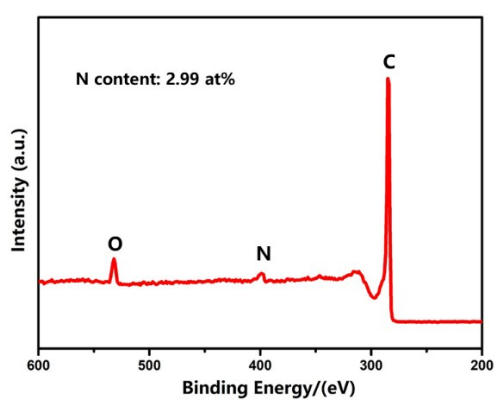
Figure S5. Full XPS spectra of N-CNF-NH$_3$.
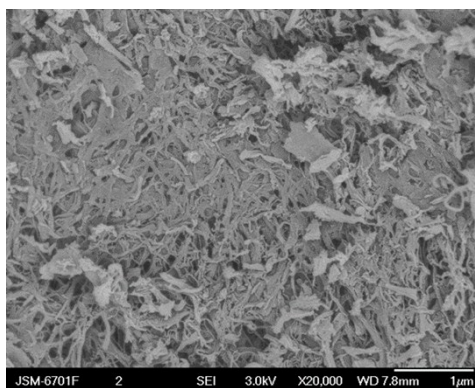
Figure S6. SEM image of N-CNF-mix.
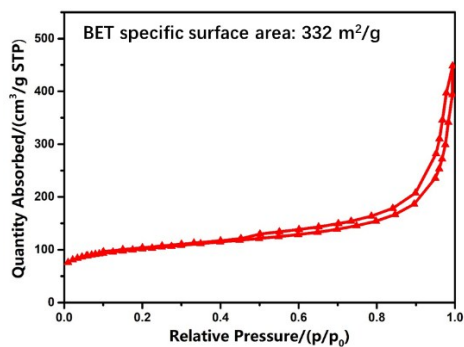
Figure S7. N_2 adsorption–desorption isotherms of N-CNF-mix.
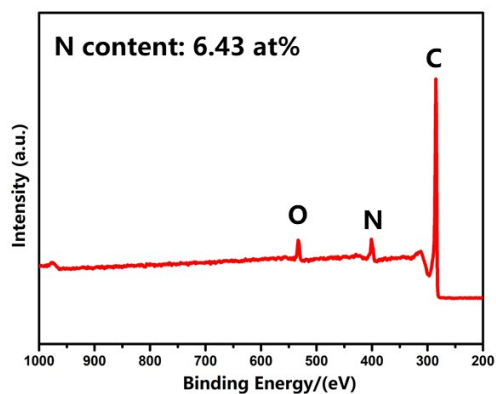
Figure S8. Full XPS spectrum XPS spectrum of N-CNF-mix.
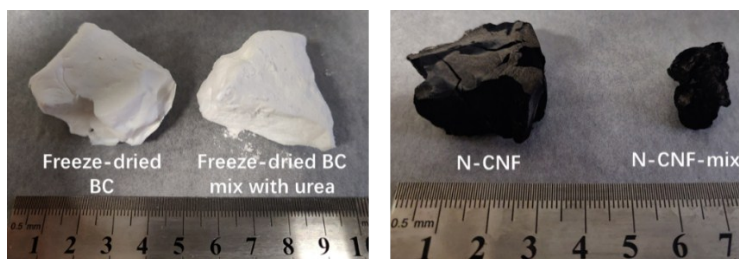
Figure S9. Digital photos of freeze-dried BC and freeze-dried BC mix with urea before and after pyrolysis.
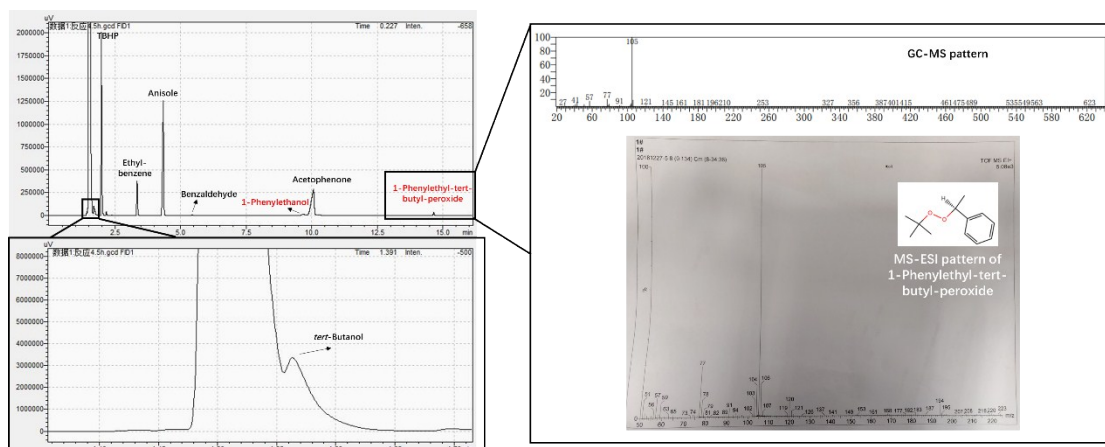
Figure S10 GC patterns of ethylbenzene oxidation reaction stopped at 4.5h, GC-MS and MS-ESI patterns of 1-phenylethyl-tert-butyl-peroxide.
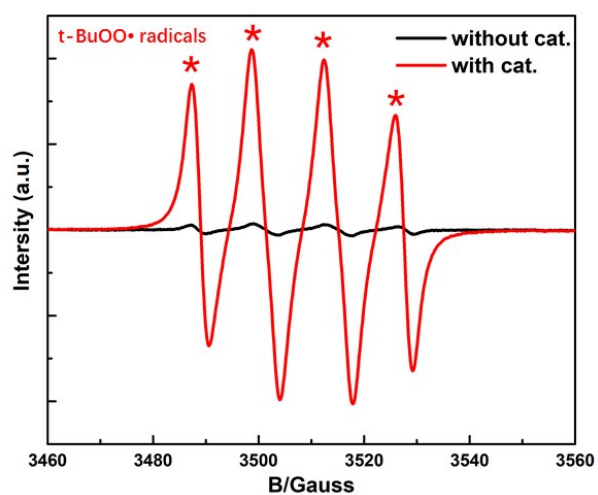
Figure S11 EPR spectra of reaction liquid mixed with DMPO.
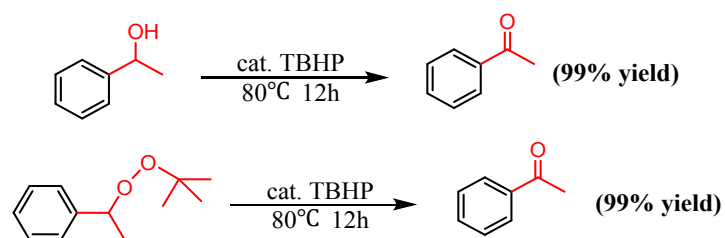
Figure S12. Two possible intermediates reacting under general reaction conditions.

$$t\text{-BuOOH} \xrightarrow{\Delta} t\text{-BuO}\cdot + \cdot\text{OH} \qquad (1)$$

$$t\text{-BuO}\cdot + t\text{-BuOOH} \longrightarrow t\text{-BuOO}\cdot + t\text{-BuOH}\ (\text{GC-MS}) \qquad (2)$$

$$t\text{-BuOO}\cdot + \text{N-CNF cat.} \longrightarrow t\text{-BuOO}\cdot^* \qquad (3)$$
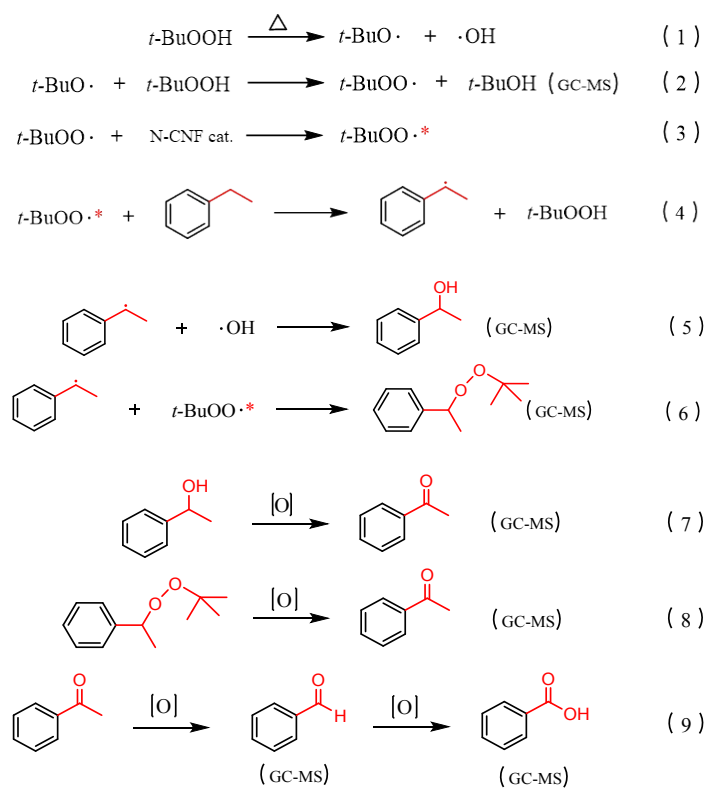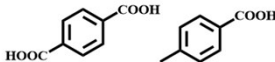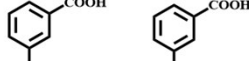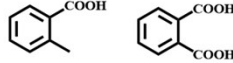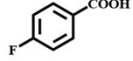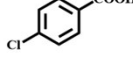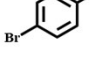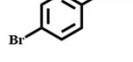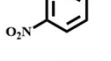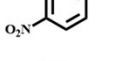
Figure S13. The proposed possible reaction mechanism.

Table S1 Comparison of catalytic performance of N-CNF for selective oxidation of ethylbenzene.

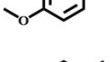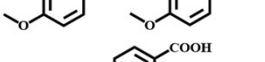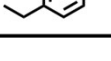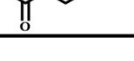| Catalyst	Reaction condition (temperature /time)	substrate/catalyst (mmol/mg)	Conversion /selectivity	Reference
N-CNF	**80ºC/12h**	**1/6**	**99%/99.2%**	**This work**
N-doped graphene	80ºC/24h	1/10	98.6%/91.3% (yield)	Angew. Chem. Int. Ed. 2013, 52, 2109.
N-doped reduced GO	80ºC/12h	1/30	99%/92%	Green Chem., 2014, 16, 3024.
Nitrogen-doped dual mesoporous carbon	70ºC/24h	1/10	88.3%/53.4% (yield)	Nanoscale, 2015, 7, 14684.
N-doped mesoporous carbon	80ºC /12h	1/20	98.5%/97.3% (yield)	Green Chem., 2016, 18, 1976.
N, P, and S-doped hollow carbon shell	80ºC /12h	1/10	99%/99.5%	Angew. Chem. Int. Ed. 2016, 55, 4016.
N, P and S co-doped carbon nanosheets	80ºC /12h	1/16	96.1%/99.1%	J. Mater. Chem. A, 2016, 4, 18470.
N, P, S-doped hollow carbon shell	80ºC /12h	1/10	94%/98.7%	Nanoscale, 2017, 9, 13538.

Table S2 Oxidation of toluene derivatives in the aqueous phase with N-CNF as catalyst. [a]

Entry	Substrate	Product	Con. (%)	Sel. (%)
1			80	95
2			95	1:2.54
3			81	1:4.39
4			94	1:2.78
5			76	98
6			67	99
7			72	99
8			43	99
9			72	1:6.58
10			99	93

[a] Reaction conditions: catalyst (5.0 mg), TBHP (500 µL, 70 wt % in water), substrate (0.5 mmol), H_2O (3.0 mL), 80 °C, 12 h.