Supplementary Information:

Atomically dispersed cobalt on graphitic carbon nitride as robust catalyst for selective oxidation of ethylbenzene by peroxymonosulfate

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Experimental Section

Materials. The materials and chemical agents in this work were supplied by Sigma-Aldrich, Australia, and were directly used without further purification.

Structure characterization. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The nitrogen adsorption-desorption isotherms were evaluated on a Micromeritics sorption analyzer (ASAP 2010) instrument at 77 K. FT-IR spectra of the samples were recorded on a Nicolet Nexus 670 spectrometer (400 to 4000 cm^{-1}). The inductively coupled plasma atomic emission spectroscopy (TJA RADIAL IRIS 1000, ICP-AES) was used to determine the mass content of cobalt. XPS measurements were conducted via a Kratos AXIS Ultra DLD system with monochromated Al Ka X-rays (1486.7 eV) operating at 225 W. The spectra were further analyzed using CasaXPS software and further calibrated by shifting the main peak in the C 1s spectrum to 284.5 eV associated with sp² carbon. X-Ray Diffraction (XRD) data were conducted by a Bruker D8 Advance diffractometer operated at 40 kV and 40 mA with Cu K α (λ = 1.5406 Å) in the range of 10-80°. The Microstructure and morphology were obtained using scanning electron microscopy (SEM, Zeiss Neon 40 EsB) and high-resolution transmission electron microscopy (HRTEM, FEI Titan G2 80-200 TEM/STEM). High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging and element mapping were collected through ChemiSTEM Technology operating at 200 kV. The elemental mapping was recorded via energy dispersive Xray spectroscopy using the Super-X detector on the Titan instrument with a probe size ~1 nm and a probe current of ~0.4 nA. High-resolution aberration-corrected scanning transmission electron microscopy annular dark field images (AC-STEM-ADF) were carried out by a Nion UltraSTEM100 microscope operating at 60 kV at a beam current of 60 pA. Near edge x-ray absorption structure (NEXAFS) spectroscopy measurements were conducted at the Soft X-Ray beamline of the Australian Synchrotron. These measurements were carried out under ultra-high vacuum (UHV) conditions with a base pressure of 5 x 10^{-10} mbar or better. All spectra were recorded in partial electron yield (TEY) mode. All NEXAFS spectra were processed and normalized using the QANT software program developed at the Australian Synchrotron. X-ray absorption spectroscopy (XAS) measurements were carried out at the XAS Beamline (12ID) at the Australian Synchrotron in Melbourne. With the beamline optics employed (Si-coated collimating mirror and Rh-coated focusing mirror) the harmonic content of the incident X-ray beam was negligible. The powder samples were made into pellets via mechanical grinding with cellulose binder using a mortar/pestle for at least 30 mins. Both fluorescence and transmission spectra were recorded based on the concentration of Co in each sample (the validity of this method was confirmed through comparing the fluorescence and transmission spectra for one of the samples for which both methods yielded comparable signal-to-noise data). All XAS data were processed on Athena software.



Fig. S1. XRD patterns of g-C₃N₄, CoNP@g-C₃N₄ and SACo@g-C₃N₄.



Fig. S2. Characterizations of $g-C_3N_4$. a) the SEM image; b) the TEM image.



Fig. S3. N₂ absorption and desorption curves of $g-C_3N_4$, CoNP@g-C₃N₄ and SACo@g-C₃N₄. The inset image is the magnified curves of $g-C_3N_4$ and CoNP@g-C₃N₄.



Fig. S4. Characterizations of CoNP@g-C₃N₄. a,b) the SEM images; c,d) the low and high resolution TEM images.



Fig. S5. XPS spectra of SACo@g-C3N4. a) whole spectrum b) C 1s c) N 1s and d) Co 2p.



Fig. S6. FTIR spectrum $g-C_3N_4$ and $SACo@g-C_3N_4$.



Fig. S7. Characterizations of CoNP@g-C₃N₄. a) the SEM image b) the TEM image c,d) HAADF image and the corresponding EDS mappings.

Entry	Catalyst	Oxidant	T (°C) ^a	Time (h)	EB	AcPO	
					conversion selectivity		Ref
					(%)	(%)	
1	Pd@N-doped carbon	$O_2/1$ atm	120	20	14.2	94	[1]
2	Co@NCNT	O ₂ /0.8 MPa	120	5	68.1	93.2	[2]
3	Carbon nanotube	O ₂ /1.5 MPa	155	4	38.2	60.9	[3]
4	Mn(III) porphyrin	$H_2O_2^c$	RT ^b	5.5	66	66	[4]
5	Co-Cu	TBHP ^d 3:1 EB(mol/mol)	120	12	92.8	89.4	[5]
6	N-porous carbon	TBHP 3:1 EB(mol/mol)	100	12	83.5	93.3	[6]
7	SACo@g-C ₃ N ₄	PMS 5:1 EB(mol/mol)	60	5	93.9	89.7	Herein
8	SACo@g-C ₃ N ₄	PMS 5:1 EB(mol/mol)	60	15	97.5	95.6	Herein

Table S1. Comparison of ethylbenzene (EB) oxidation via different reaction systems.

^a Reaction temperature.

^b Room temperature

^c Aqueous hydrogen peroxide (30% w/w) was diluted in acetonitrile (2:5) and added to the reaction mixture in 37.5 μ l aliquots every 15min for the oxidation of 0.3mmol ethylbenzene.

^d *Tert*-butyl hydroperoxide





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