Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Noncovalent functionalization of multi-walled carbon nanotubes as metal-free catalysts for the reduction of nitrobenzene

Xianmo Gu,[a,b] Wei Qi,[b] Shuchang Wu,[b] Zhenhua Sun,[b] Xianzhu Xu,*[a] Dangsheng Su*[b]

[a] *State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, P. R. China; Tel: +86 451 86403715 Fax: +86 45186403625;*

E-mail: xuxianzhu@hit.edu.cn (X. Z. Xu)

[b] *Shenyang National Laboratory for Material Science,Institute of Metal Research, Chinese Academy of Sciences, 110016 Shenyang, People's Republic of China*

E-mail: dssu@imr.ac.cn(D. S. Su)

Experimental section

Materials: Commercial CNTs used in present work are purchased from Pyrograf Products Inc. (Ohio, USA). The grade of the sample is XT-HHT. We label the CNTs as HHT. They are prepared by chemical vapor deposition (CVD) and subsequently heat-treated at 3000°C under nitrogen by provider. Some basic physicochemical data is given on the company website. All chemicals are of analytical grade and are used as received without further purification.

***Purification of HHT*:** 5g HHT was dispersed in concentrated hydrochloric acid (500 ml) under ultrasonication for 15 min and then stirred at room temperature for 24 h. After treatment, the solution was filtered and the sample was thoroughly rinsed with deionized water until pH equaled to 6-7. The resulting black solid was dried in a vacuum oven at 100 °C overnight, and the sample was labeled as NF-HHT.

***Synthesis of catalysts by liquid phase method*:** 200 mg NF-HHT was dispersed in 100 ml N, N-dimethylformamide (DMF) in two-neck flask through 30 min ultrasonication. Afterwards, 50 ml DMF solution containing 1 g phenanthrenequinone (PQ) was added dropwise. The mixture was stirred at 160 °C for 48 h. After cooling to room temperature, the crude was filtrated. Then the product was removed from the filter and washed with DMF and ethanol (sonicated and filtrated) until the filtrate was clear. The resulting black sample was dried in a vacuum oven at 100 °C overnight, and the sample was labeled as LF-HHT-PQ.

***Synthesis of catalysts by solid phase method*:** The phenantraenequinone (300 mg) and NF-HHT (150 mg) were mixed using a mortar, and the resulted powder was transferred in a fixed bed quartz glass tube reactor operating at ambient pressure. The reaction mixture was heated at 220 °C for 8h under an argon flow (50 ml min^{-1}). After cooling to room temperature, the solid residue was subjected to soxhlet extraction with ethanol for 3 days and dried in a vacuum oven at 100 °C overnight. The resulting sample was labeled as SF-HHT-PQ. HHT-AQ and HHT-AR were fabricated through similar solid phase method with anthraquinone (AQ) and anthrone (AR) as precursors.

***Catalysis test*:** The catalyst (10 mg), nitrobenzene (0.5 ml), hydrazine hydrate (85 %, 2 ml), and 1.5 ml ethanol were added in turn into a 25 ml round-bottom flask. The reaction mixture was stirred at 100 °C for certain time. When the reaction was finished, the mixture was diluted exactly to 50 ml in a volumetric flask with methanol aqueous solution (75%). The products were analyzed by HPLC (Elite, UV detector, mobile phase: 3/1 (v/v) methanol/water) with SinoChrom ODS-BP column. The conversion (Con.) of reactant, the selectivity (Sel.), the yield of products and the TOF of catalyst were obtained by the following equations:

$$\mathrm{Con.}(\%) = \frac{n_1}{n_0} \times 100\%; \ (1)$$

$$\mathrm{Sel.}(\%) = \frac{n_2}{n_1} \times 100\%; \ (2)$$

$$\mathrm{Yield}\ (\%) = \mathrm{Con.}(\%) \times \mathrm{Sel.}(\%); \ (3)$$

$$\mathrm{TOF}(h^{-1}) = \frac{n_0(Y_1 - Y_0)}{n_{cat.} \times C{=}O(\mathrm{atom}\%) \times \mathrm{Time}}; \ (4)$$

(n_0 is the initial moles of reactant; n_1 is the moles of reactant converted; n_2 is the moles of products formed; Y_1 is the aniline yield for the catalytic process; Y_0 is the aniline yield for blank test; n_{cat} is the moles of the catalyst.)

***Characterization*:** Thermogravimetric (TG) was performed on NETZSCH STA 449 F3 under a flow of argon (50 ml min^{-1}) with a heating rate of 3°C min^{-1} from 35 to 800 °C. The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) ESCALAB 250 set-up equipped with a monochromatic Al Kα X-ray source (1486.6eV; anode operating at 15kV and 20mA). The peak was calibrated based on the C1s peak of graphitic carbon (284.6 eV). The O1s XPS spectra were fitted using mixed Gaussian-Lorentzian component profiles (at a ratio of 80/20 - 60/40) after subtraction of a Shirley background using XPSPEAK41 software. The fitting was performed by fixing the peak position for individual species within 0.1 eV and applying a full width at half-maximum (FWHM) of 1.2 -1.6 eV. Raman spectroscopy was performed on a LabRam HR 800 by using a 633 nm laser.

Table S1 Summary of XP O1s spectra data.

Sample	**XPS** (atom%)			**C=O** (atom%)[a]	**C-O** (atom%)[a]	
	C	N	**O**	**O1**(531.5±0.1)[b]	**O2**(532.6)[b]	**O3**(533.7±0.1)[b]
				(1.35)[c]	(1.4)[c]	(1.55)[c]
NF-HHT	97.07	1.59	1.34	**0.17**	0.66	0.51
LF-HHT-PQ	95.98	2.14	1.88	**0.33**	0.63	0.92
SF-HHT-PQ	95.25	1.62	3.10	**0.78**	1.09	1.23
SF-HHT-PQ-1[d]	92.86	1.58	5.56	**1.04**	2.41	2.12
HHT-AQ-1[e]	91.66	1.31	7.04	**0.24**	3.37	3.43
HHT-AQ-2	95.64	1.58	2.78	**0.69**	1.16	0.92
HHT-AQ-3	95.77	1.59	2.64	**0.80**	1.08	0.76
HHT-AR[f]	95.26	1.95	2.79	**0.80**	1.06	0.93

a the surface atomic concentrations of oxygen are calculated from the corresponding peaks areas of the XP O1s spectra; b. the binding energy of oxygen species; c the FWHM of the deconvoluted O1s bands; d. SF-HHT-PQ-1 stands for the catalyst prepared using similar solid phase method by increasing the weight ratio of reactants; e. HHT-AQ-n (n=1, 2, 3) stands for the HHT functionalized by Anthraquinone (AQ) under different temperature. The temperature used for the functionalization of HHT-AQ-1, HHT-AQ-2 and HHT-AQ-3 is 360, 300 and 260 °C, respectively; f. HHT-AR stands for the HHT functionalized by Anthrone (AR);

Table S2 Sample denotations and comparison of the fit parameters from the peaks fitted in the Raman spectra of CNT samples.

Sample	Description	Position [cm^{-1}]	Area (a.u.)	FWHM [cm^{-1}]	**I_D/I_G**
NF-HHT	D	1332.4	12.2	18.8	**0.39**
	G	1578.2	30.9	11	
	D’	1616.2	2.05	6.95	
LF-HHT-PQ	D	1330.2	16.5	18.9	**0.44**
	G	1576.6	37.7	12.2	
	D’	1613.6	2.9	7.9	
SF-HHT-PQ	D	1328.9	22.7	19.8	**0.49**
	G	1575.4	46.3	14.2	
	D’	1614	2.14	6.99	

Tables S3 Reaction data of all the tested catalysts.

Catalyst	Reaction time (h)	Con. (%)	Sel. (%)	Yield (%)
NF-HHT	3	15.5	100	15.5
	6	33.5	93.9	31.5
	9	51.5	100	51.5
	12	61.7	100	61.7
	15	81.5	100	81.5
	18	94.4	100	94.4
	21	97.4	100	97.4
LF-HHT-PQ	3	21.9	92.8	20.3
	6	45.2	95.9	43.3
	9	56.4	100	56.4
	12	74	100	74
	15	96.6	100	96.6
	18	97.6	100	97.6
SF-HHT-PQ	3	37.6	99	37.2
	6	61.8	100	61.8
	9	76.5	100	76.5
	12	90.8	100	90.8
	13	97.5	100	97.5
SF-HHT-PQ-1	3	45.4	100	45.4
	6	72	100	72
	9	85.9	100	85.9
	12	98.3	98.7	97
HHT-AQ-1	6	40.7	100	40.7
HHT-AQ-2	6	49.7	100	49.7
HHT-AQ-3	6	53.3	100	53.3
HHT-AR	6	38.1	100	38.1

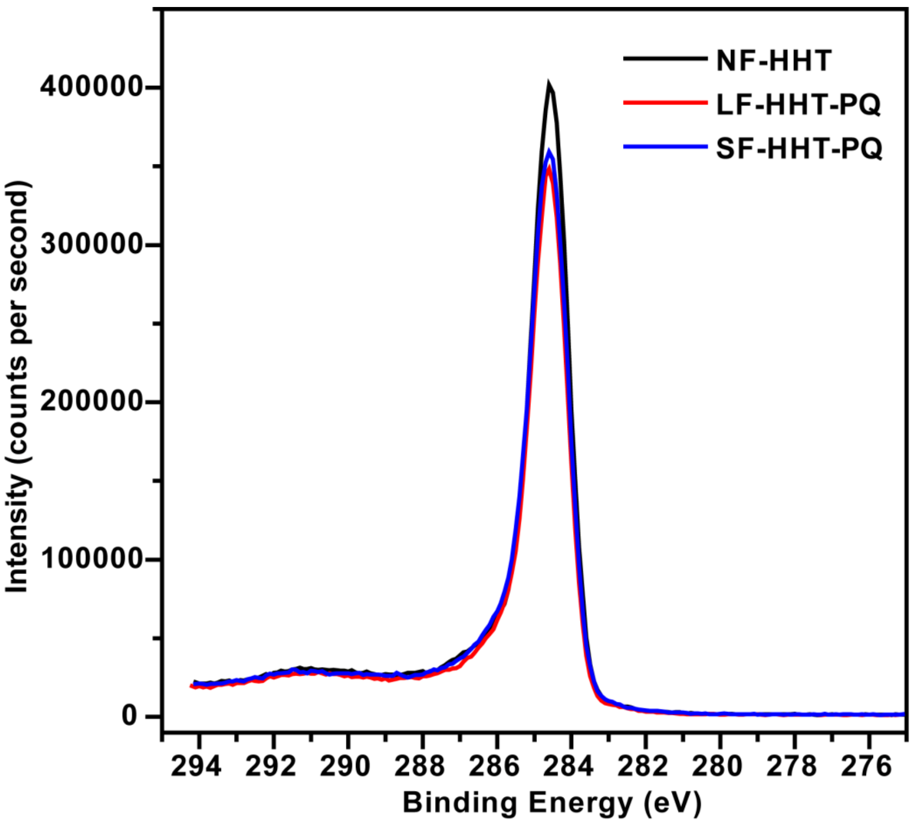

Figure S1 XP spectra of the C1s for NF-HHT, LF-HHT-PQ and SF-HHT-PQ

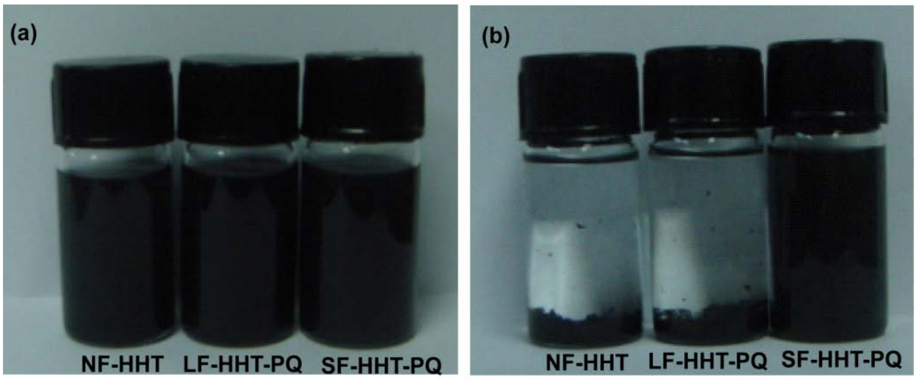

Figure S2 Photograph of solutions of NF-HHT, LF-HHT-PQ and SF-HHT-PQ dispersed in ethanol (0.05g/L) after ultrasonification (a) and overnight (b).

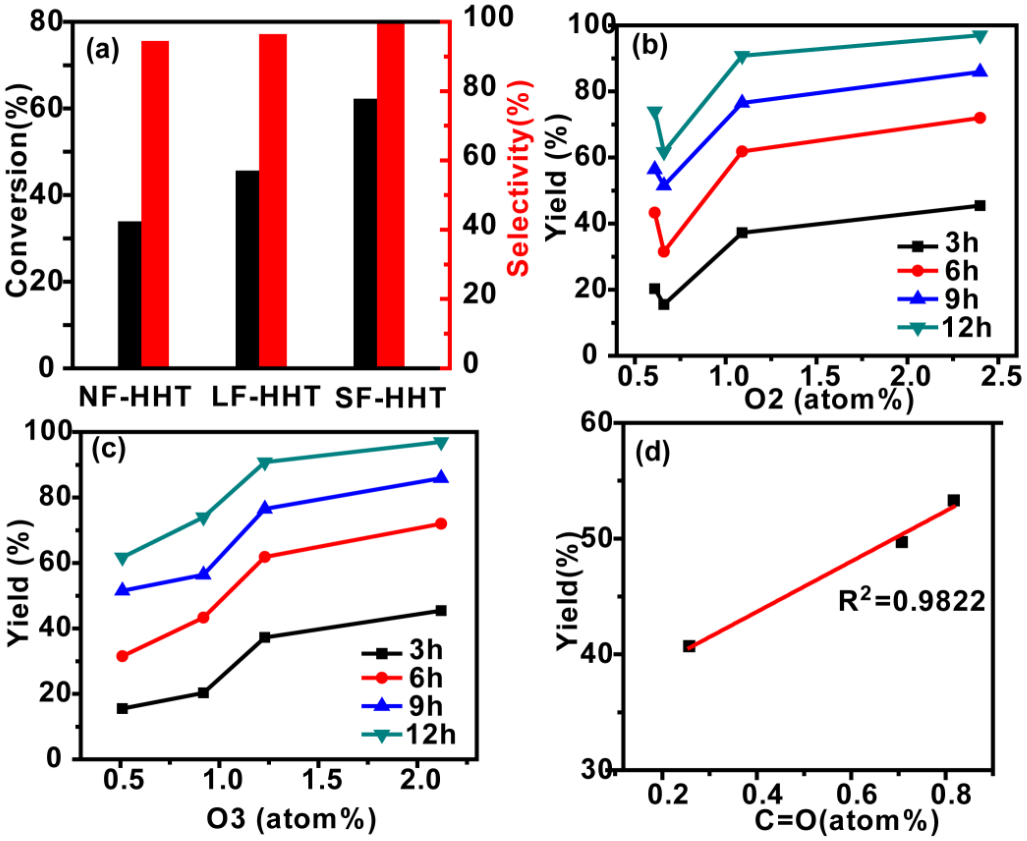

Figure S3 (a) The conversion and selectivity of NF-HHT, LF-HHT-PQ and SF-HHT-PQ at the reaction time of 6 h; (b) The yield of aniline as a function of atomic percent of O2 species in different reaction times (c) The yield of aniline as a function of atomic percent of O3 species in different reaction times (d) The yield of aniline as a function of atomic percent of C=O when HHT-AQ-n (n=1, 2, 3) were used as catalyst in the reduction of nitrobenzene at 6h.

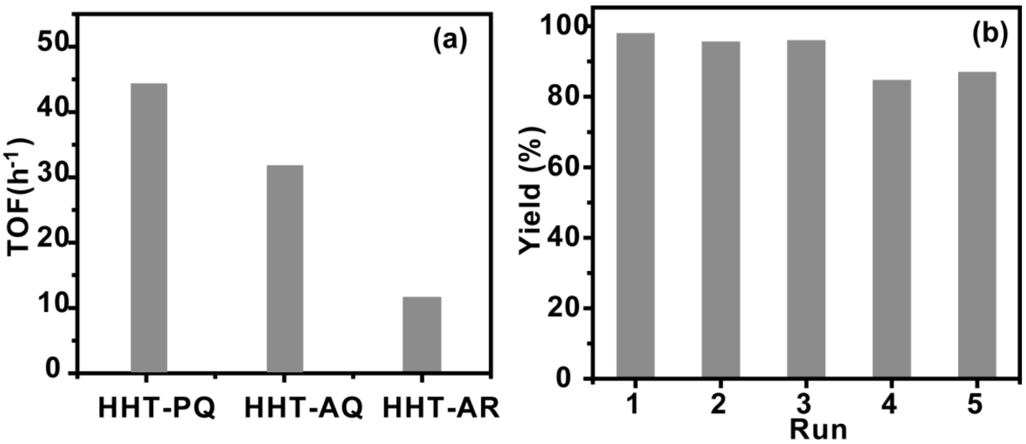

Figure S4 (a) The TOF of different catalysts; (b) Cycle performance test of SF-HHT-PQ catalyst for the reaction of nitrobenzene to aniline for 13h.