Electronic Supplementary Information

Structure and Catalytic Activities of Ferrous Center Confined on the

Interface between Carbon Nanotube and Humic Acid

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METHODS

XAS data processing. The collected Fe XAS spectra were analyzed with Athena 0.8.061 software. Spectra processing includes energy calibration, background correction, normalization, derivative and linear combination fit. EXAFS oscillations were extracted from XAS data using a standard procedure of Athena program and EXAFS modeling was performed with the program ARTEMIS. The theoretical backscattering amplitudes and phase shifts were calculated with FEFF 8.2. The best-fit distances, coordination numbers, and Debye-Waller factor was obtained from thefirst shell fits to κ^2 weighted Fourier transform EXAFS data. The collected C XAS spectra were normalized with the incident photon flux measured as drain current at the focusing mirror.

Theoretical calculation. The program Gaussian 09 has been employed to carry out all the calculations, and all data reported here are from the calculations with solvent effect included. In the calculations, the nanotube was simulated by a 1-nm CNT[5,5] with both terminals saturated by hydrogen atoms, and humic acid was modelled by several model compounds to represent its lipophilic and hydrophilic structure units respectively. The "Inner region" highlighted in the structure of CNT[5,5] has been used to analyze the fluctuation of atomic charges of a nanotube upon the binding of ligand and/or Fe^{3+} cation.

EPR measurement. Production of O_2 and OH was measured using the 1-hydroxy-3carboxy-pyrrolidine (CPH) and 5.5-dimethyl-1-pyrroline N-oxide (DMPO) as their respective spin probes. CPH, as the spin traps of superoxide anion radical ($^{\circ}O_{2}^{-}$), can react with O_2^- to form stable spin label CP* with a typical EPR spectrum of three lines. A reaction mixture for EPR analysis contained 0.05 mM CPH and a certain concentration of samples was measured. 5.5-dimethyl-1-pyrroline N-oxide (DMPO) was used to trap and stabilize •OH as spin adduct DMPO/•OH, giving a characteristic EPR spectrum of 4 lines with an intensity ratio of 1:2:2:1. A reaction mixture consisted of 50 mM DMPO, 0.5 mM H₂O₂, and a certain concentration of samples (400 ppm HA-Fe, 100 ppm HA/Fe-CNT, or 100 ppm CNT-Fe). All EPR measurements were carried out using a Bruker EMX EPR Spectrometer (Bruker Biospin, Billerica, MA). The EPR instrument settings were 20 mW microwave power, 100 G scan range and 1 G field modulation, 40 s scan time, and number of scans = 9. The measurements were performed in replicates at ambient temperature. All of the chemical agents used in EPR were purchased from Sigma-Aldrich, USA.

Oxidative degradation of PR and BPA. UPLC analysis was conducted using a C18 reverse column (Acquity UPLCTM BEH, C18, (1.7 μ m, 2.1×100 mm). Mobile phases consisted of 90% methanol containing 0.1% ammonium hydroxide (A) and 10% methanol containing 0.1% ammonium hydroxide (B). The UPLC system operated at isocratic mode (70% methanol) with a flow rate of 0.3 mL/min. The peak of BPA and degraded products was detected at 265 nm. The instrument parameters of mass spectrometer were as follows:

capillary voltage: 3.2 kV; cone voltage: 40 kV; Nebulizer: 0.7 bar, dry temperature: 180 °C, dry gas: 4.01/min. Spectra were acquired in positive ion mode with a scan range of 50–1500 m/z. The accurate mass data of molecular ions were processed with the Data Analysis 4.0 Software.

	Fe 2p _{3/2} BE (eV)		Fe 2p _{1/2} BE (eV)		
Fe 2p	Fe (II)	Fe (III)	Fe (II)	Fe (III)	Fe(II)/ ∠ Fe (%)
	712.2	710.8	723.8	725.0/726.5	44.9

Table S1 Multiplets for the Fe $2p_{_{3/2}}$ and Fe $2p_{_{1/2}}envelope$



(a) 100 ppm CNT; (b) CNT/HA (W/W, 1:2)

Fig. S1. Physicochemical properties of CNT-HA complex. SEM image of CNT dispersed in water (a) and HA system (b). UV-Vis spectrum of CNT-HA complex (c). Raman spectrum of CNT-HA complex (d). FTIR spectrum of CNT-HA complex (e). SRXPS survey spectra

(f) and quantitative analysis of C chemical state (g) in CNT-HA complex.



Fig. S2. Effects of CNT/HA ratio on surface C chemical states of CNT-HA complex. The high-resolution XPS analysis of C1s spectrum shows the contents of C-OH, -C=O and -COOH in CNT-HA complex are related to HA/CNT mass ratio. When the mass ratio of HA/CNT increased to 2:1, the content of O-containing functional groups, including -OH, -C=O and -COOH, increased to 24.0%, 4.8%, 6.8%, respectively, which are beneficial for the Fe loading into CNT-HA *via* Fe-O coordination.



Fig. S3. Effects of pH on surface C chemical states of CNT-HA complex. The content of O-containing groups in CNT-HA complex ranged from 76.7% to 67.7% at pH 3.6-10.1, indicating that the CNT-HA had a potential to load Fe in a very wide pH range.



Fig. S4 Models used in the calculations: the 1-nm-long CNT[5,5] and the model compounds used to represent fragmented parts of a humic acid molecule (molecular charge given in parenthesis).



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Fig. S5. Oxidatiion degradation of PR and BPA by HA/Fe-CNTs catalysis. Oxidation of PR by HA/Fe-CNTs complex (a) and pH independent oxidation of PR (b). ESI-Mass spectrum of BPA (c) and its oxidation products (d). Reaction rate constant of BPA degradation (e).



Fig. S6 Recovery of the HA/Fe-CNT catalysts during 3 consecutive running cycles.