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Interaction of surface electron distribution-polarized Fe/polyimide hybrid nanosheets with organic pollutants driving sustainable Fenton-like process

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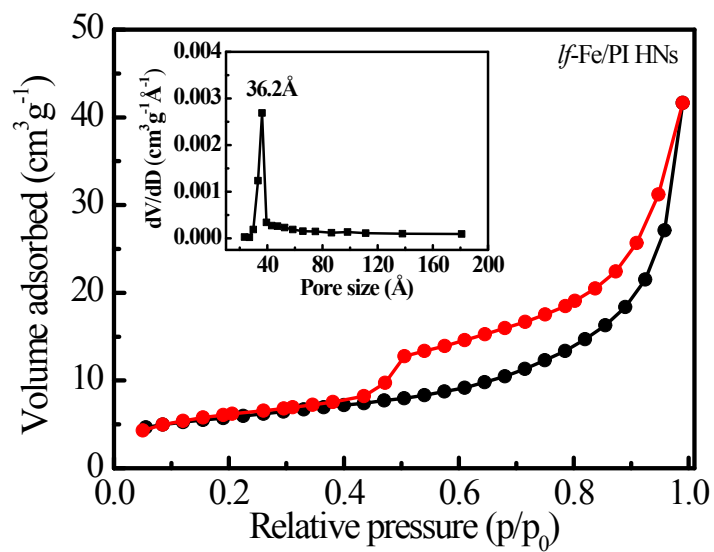
Pages 12, Figures 6, Notes 4

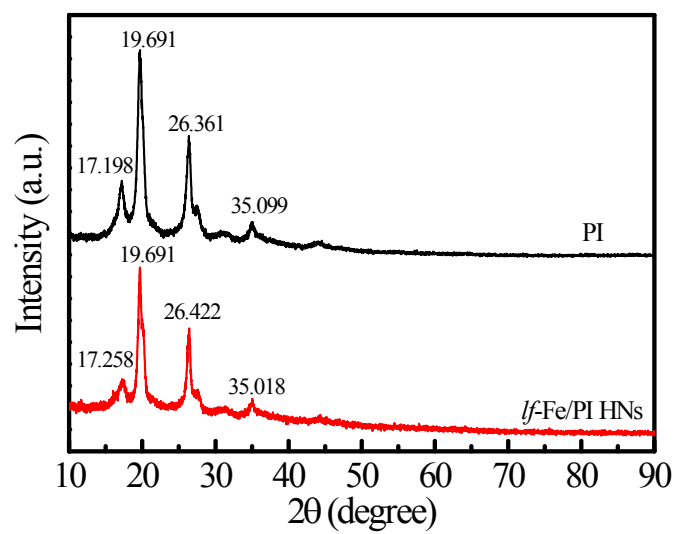**Fig. S1. N$_2$ adsorption-desorption isotherms and BJH pore size distribution (inset) of *lf*-Fe/PI HNs.**

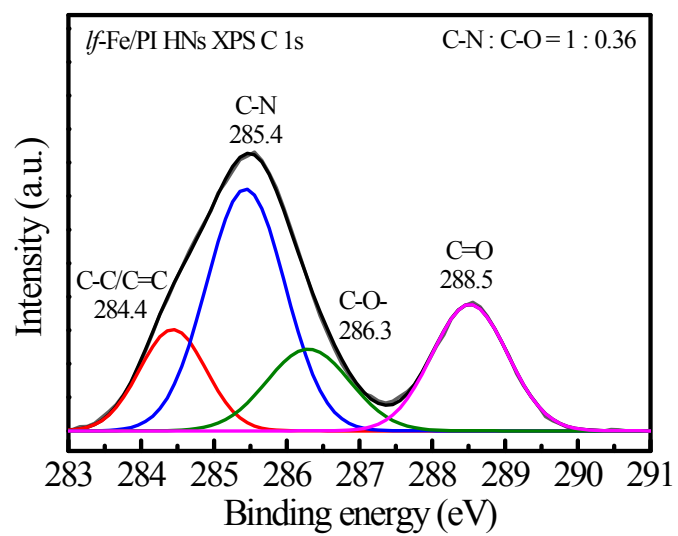**Fig. S2. XRD patterns of PI and *lf*-Fe/PI HNs.**

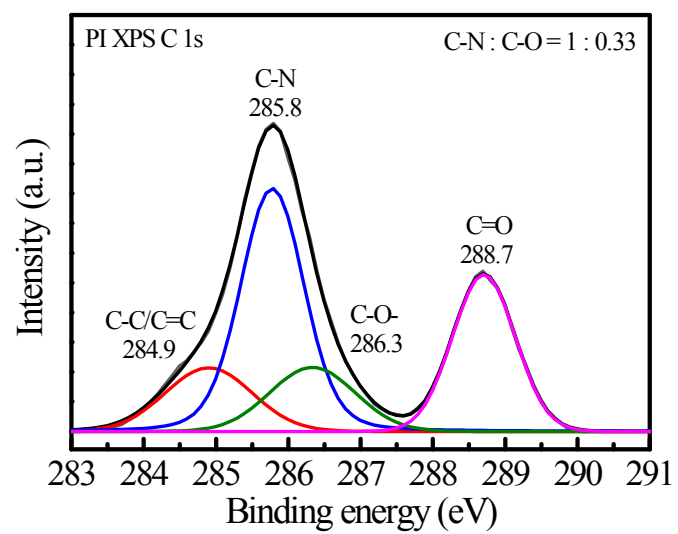**Fig. S3. C 1s XPS spectrum of *lf*-Fe/PI HNs.**
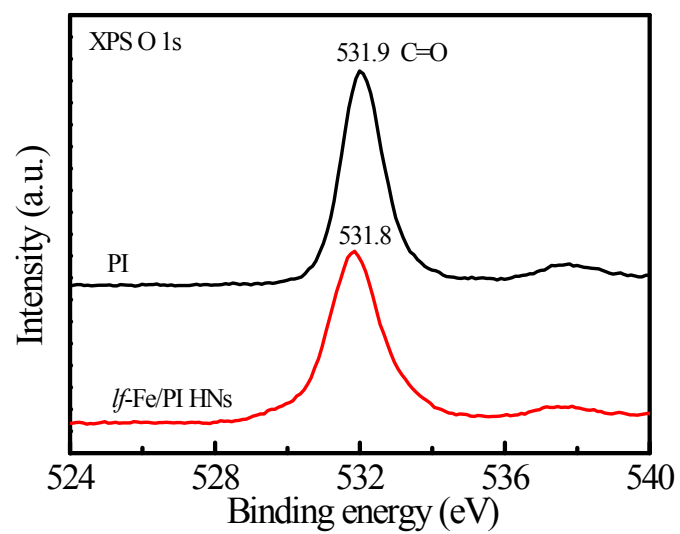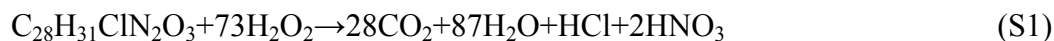
Fig. S4. C 1s XPS spectrum of PI.

Fig. S5. O 1s XPS spectra of PI and *lf*-Fe/PI HNs.

Notes S1. Calculation of the utilization efficiency of H_2O_2.

The complete mineralization of one mole of RhB will theoretically consume 73 moles of H_2O_2 (eqs. S1).

$$C_{28}H_{31}ClN_2O_3 + 73H_2O_2 \rightarrow 28CO_2 + 87H_2O + HCl + 2HNO_3 \qquad (S1)$$

The utilization efficiency of H_2O_2 (η) is defined as the ratio of the stoichiometric consumption of H_2O_2 ($[\Delta H_2O_2]_S$) for the mineralization of pollutants to the actual consumption of H_2O_2 ($[\Delta H_2O_2]_A$) in the Fenton-like reaction[1] and is expressed in eq. S2:

$$\eta = [\Delta H_2O_2]_S / [\Delta H_2O_2]_A \qquad (S2)$$

By measuring the TOC change in the pollutant solutions, the amounts of the mineralized contaminants were obtained, and the value of $[\Delta H_2O_2]_S$ was calculated. The actual consumption of H_2O_2 ($[\Delta H_2O_2]_A$) at different reaction times was measured using the DPD method.[2] The detailed data for $[\Delta H_2O_2]_A$ and $[\Delta H_2O_2]_S$ are presented in the following Table.

Stoichiometric consumption of H_2O_2 ($[\Delta H_2O_2]_S$) and actual consumption of H_2O_2 ($[\Delta H_2O_2]_A$) for mineralizing RhB during the Fenton-like reaction.

Reaction time/min	RhB (10 mg L^{-1})	
	$[\Delta H_2O_2]_S$/mM	$[\Delta H_2O_2]_A$/mM
0	0	0
30	0.370	0.459

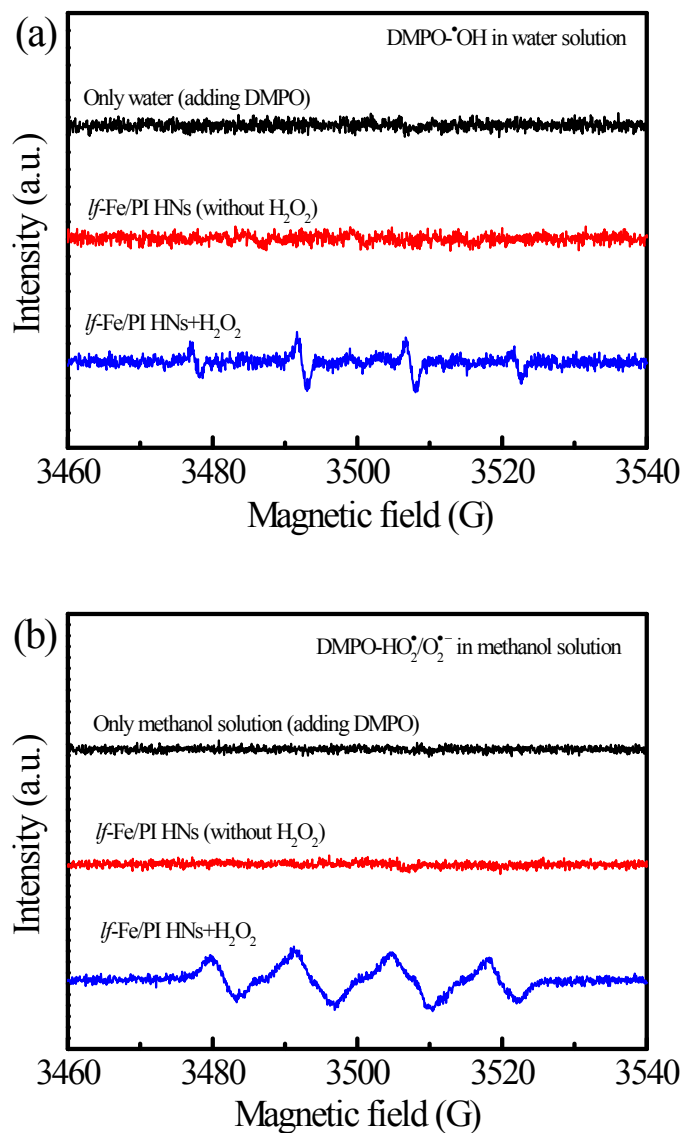|		
60	0.502	0.663
90	0.691	1.020
120	0.768	1.173

Fig. S6. Free radical detection in different solutions. DMPO spin-trapping EPR spectra for **a** $^{\bullet}OH$ in various aqueous suspensions and **b** $HO_2^{\bullet}/O_2^{\bullet-}$ in various methanol suspensions.

Notes S2. Chemicals and reagents

5,5-Dimethyl-1-pyrroline N-oxide (DMPO, >98%), *N,N*-diethyl-*p*-phenylenediamine sulfate (DPD, 99%), rhodamine B (RhB, 96%), acid orange 7 (AO7, 99%), bisphenol A (BPA, >98%), 2-chlorophenol (2-CP, 99%), ethylenediamine (EDA, 99%) and pyromellitic dianhydride (PMDA, >98%) were purchased from Adamas Reagent Co., Ltd. (Switzerland). Horseradish peroxidase (POD, 99%) and ciprofloxacin (CIP) were purchased from TCI (Shanghai) Development Co., Ltd. N,N-Dimethylformamide (DMF, ≥99.8%), ferric chloride (FeCl$_3$, ≥99%) and glucose (AR) were obtained from Shanghai Titan Scientific Co., Ltd (Shanghai, China). Hydrogen peroxide (H$_2$O$_2$, 30%, w/w) and all the other chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Deionized water was used throughout this study.

Notes S3. Procedures and analysis

The concentrations of RhB and AO7 were measured by the Hitachi Model UH4150 Spectrophotometer. The concentrations of BPA, 2-CP and CIP were measured by a high performance liquid chromatography (HPLC, 1260 Infinity II; Agilent) with an auto-sampler, a Poroshell 120 EC-C18 column (4.6 × 100 mm, 2.7 μm) and an UV detector. The mobile phase was a mixture of methanol/water and was operated at a flow-rate of 1.0 mL min^{-1}. The total organic carbon (TOC) was determined by a TOC-L CPH CN200 analyzer (Shimadzu) using high-temperature combustion. The H_2O_2 concentration was determined using the reported DPD method.[1] The amount of metallic ions releasing from the catalysts during the reaction were measured using the inductively coupled plasma mass spectrometry (ICP-MS) on a NexION 300 (PerkinElmer, U.S.A.). DMPO-trapped EPR signals were detected in different air-saturated methanol/aqueous dispersions of the corresponding samples. The EPR spectra were recorded on a Bruker A300-10/12 EPR spectrometer at room temperature. Typically, 0.01 g of the prepared powder sample was added to 1 mL of water (for detecting $^{\bullet}OH$) or methanol (for detecting $O_2^{\bullet-}$). Then, 100 μL of the above suspension, 10 μL of H_2O_2 (30%, w/w, if needed) and 20 μL of DMPO were mixed and held for 1 min. The solution was sucked into the capillary to carry out EPR detection.

Notes S4. Computational methods of density functional theory (DFT)

The optimization of geometry and wave function was performed using B3LYP functional and 6-31G(d) basis set with the Gaussian 09 package. The valence-electron density was analyzed with the Multiwfn package. The dangling bonds were terminated with H atoms to obtain a neutral cluster. Due to the size and edge effects, the properties estimated with the finite-size model may vary from those of the real system to some extent. However, the results obtained with the current model would be qualitatively reliable in predicting the local chemical properties.

References

1.   Luo, W.; Zhu, L. H.; Wang, N.; Tang, H. Q.; Cao, M. J.; She, Y. B., Efficient Removal of Organic Pollutants with Magnetic Nanoscaled BiFeO3 as a Reusable Heterogeneous Fenton-Like Catalyst. *Environ Sci Technol* **2010,** *44*, (5), 1786-1791.

2.   Bader, H.; Sturzenegger, V.; Hoigne, J., Photometric-Method for the Determination of Low Concentrations of Hydrogen-Peroxide by the Peroxidase Catalyzed Oxidation of N,N-Diethyl-P-Phenylenediamine (DPD). *Water Res* **1988,** *22*, (9), 1109-1115.