Supporting information

Phosphorus-induced Electronic Coupling between Fe Single Atoms and Fe_2O_3 Nanoparticles on Biomass-Derived Carbon for Efficient Oxygen Reduction

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Material

Poly(diphenoxyphosphazene) (97%, Bide Pharm), Saccharum officinarum residue (Nanning, Guangxi), acetone (99.5%, Chengdu Kelong Chemical Co., Ltd.), iron(III) nitrate nonahydrate (AR, Tianjin Damao Chemical Reagent Factory), isopropanol (99.5%, Xilong Scientific Co., Ltd.), 20 wt% Pt/C (Johnson Matthey), 5 wt% Nafion solution (Energy Chemical), potassium hydroxide (85%, Aladdin).

Characterization

The corresponding characterizations of catalysts were performed with the equipment as following: Oxygen Nitrogen Hydrogen Analyzer (ONH-2000, ELTRA GmbH, Germany); Inductively Coupled Plasma Optical Emission Spectrometer (ICAP PRO, Thermo Fisher Scientific Inc.); Raman Spectrometer (Dxr2xi, Thermo Fisher Scientific Inc.); Specific Surface Area and Porosity Analyzer (ASAP 2460, Micromeritics Instrument Corporation, USA); X-ray Diffractometer (Miniflex 600-C, Rigaku Corporation, Japan); X-ray Photoelectron Spectrometer (K-AlphaTM+, Thermo Fisher Scientific Inc.); Spherical Aberration Transmission Electron Corrected Scanning Microscope (JEM-ARM200F, JEOL Ltd., Japan); Scanning Electron Microscope (Phenom KL G2, Thermo Fisher Scientific Inc.); Transmission Electron Microscope (F200X G2).

Synthesis of Catalysts

Preparation of activated carbon from saccharum officinarum residue

The Saccharum officinarum residue was washed to remove contaminants and dried at 105 ℃ for 24 hours. Then the dried residue powder was placed into a tubular furnace (GSL-1100X, Hefei Kejing Materials Technology Co., Ltd.). After vacuuming 5-6 times, nitrogen gas was introduced at 30 mL/min. The tubular furnace was then raised to 900 ℃ at 5 ℃/min, then maintained for 3 hours. After cooling the tube furnace to room temperature, the activated carbon powder was obtained.

Synthesis of P-C Material

30 mL acetone, 0.5 g activated carbon and 2 g poly(diphenoxyphosphazene)

were added into a beaker, then stirring for 4h. After removing the solution under vacuum, the mixture was transferred into a tubular furnace. Subsequently, the mixture was pyrolyzed at 900 ℃ for 3h, with 5 ℃/min and 30mL/min N_2, which yielded the P-C material.

Synthesis of Fe-P-C-T Catalyst

0.89 g P-C powder, 0.05 of $Fe(NO_3)_3$ and 10 mL acetone were mixed for 4 hours. After removing the solution under vacuum, the mixture was transferred into a tubular furnace. Subsequently, the mixture was pyrolyzed for 3h at various temperatures with 5 ℃/min and 30mL/min N_2, which yielded the Fe-P-C-T catalyst (T denotes the temperature).

Synthesis of Fe NPs/P-C

0.89 g P-C powder, 0.2 g $Fe(NO_3)_3$ and 10 mL acetone were mixed for 4 hours. After removing the solution under vacuum, the mixture was transferred into a tubular furnace. Subsequently, the mixture was pyrolyzed for 3h at 1000 ℃ with 5 ℃/min and 30mL/min N_2, which yielded the Fe NPs/P-C.

Electrocatalytic oxygen reduction performance test

The electrocatalytic oxygen reduction performances of catalysts were tested using a Pine bipotentiostat and a three-electrode system (working electrode: 5.0 mm rotating disk electrode (RDE), reference electrode: Ag/AgCl electrode, counter electrode: 3.0 mm graphite carbon rod) in 0.1 M potassium hydroxide electrolyte at room temperature.

Preparation of 5.0 mm RDE working electrode: Mix 2 mg Fe-P-C-T catalyst, 400 μL isopropanol, and 20 μL 5 wt% Nafion solution in a 1.5 mL sample vial, and ultrasonicate for 3-4 hours until a uniform ink-like dispersion is achieved. Subsequently, 10 μL of the freshly prepared ink suspension is drop-cast onto the polished RDE surface and allowed to dry naturally.

In an oxygen-saturated 0.1M KOH solution, CV curves were obtained by scanning 30 cycles at a scan rate of 100 mV/s within a voltage range of 0.2V to -0.8V

using a 5.0mm RDE working electrode. Subsequently, measurements were conducted at a scan rate of 10 mV/s with rotation speeds of 400 rpm, 625 rpm, 900 rpm, 1225 rpm, 1600 rpm, 2025 rpm, and 2500 rpm. After completing all rotation speed tests, nitrogen saturation was applied to measure and subtract the background current, yielding the LSV curve. The current densities at standard hydrogen electrode potentials of 0.40V, 0.44V, 0.48V, 0.52V, and 0.56V were selected from the LSV curve, and the electron transfer number was calculated using the K-L equation.

Prepare the rotating ring-disk electrode (RRDE) working electrode: Mix 2 mg of Fe-P-C-T catalyst, 400 μL of isopropanol, and 20 μL of 5 wt% Nafion solution in a 1.5 mL sample vial, then ultrasonicate for 3-4 hours until a uniform ink-like dispersion is achieved. Subsequently, deposit 10 μL of the freshly prepared ink suspension onto the polished RRDE surface and allow it to dry naturally.

In an oxygen-saturated 0.1M KOH solution, the RRDE working electrode was tested within a voltage range of 0.2V to -0.8V at a scan rate of 10 mV/s and a rotation speed of 1600 rpm. Subsequently, the background current was subtracted under nitrogen-saturated conditions to obtain the electron transfer number and hydrogen peroxide yield.

Tabel S1 Elements analysis of Fe/P-C-1000

Catalyst	**Metal (wt%)[a]**	**Phosphorus (wt%)[a]**	**Nitrogen (wt%)[b]**
Fe/P-C-1000	0.384	3.06	0.6212

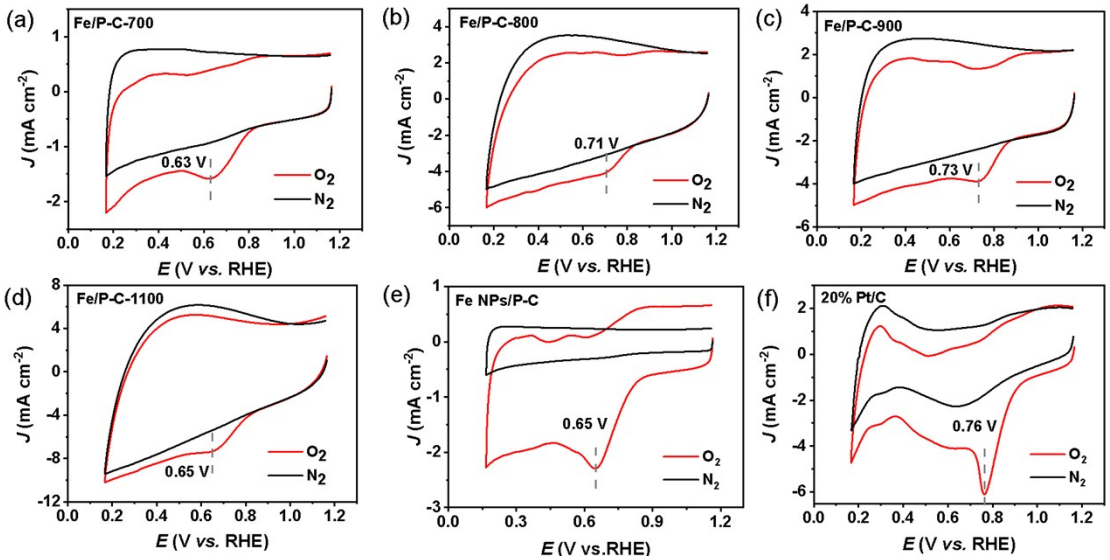

Figure S1. Cyclic voltammetry curves of catalysts recorded in an O_2-saturated 0.1 M KOH solution: (a) Fe/P-C-700, (b) Fe/P-C-800, (c) Fe/P-C-900, (d) Fe/P-C-1000, (a) Fe NPs/P-C-1000, and (f) 20% Pt/C.

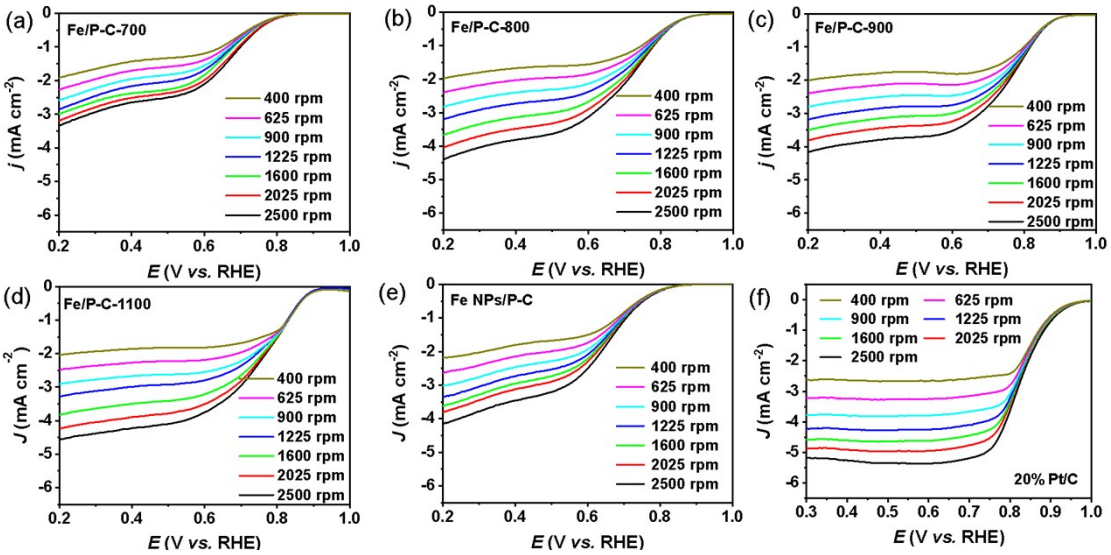

Figure S2. LSV curves for ORR of catalysts and 20 wt% Pt/C in O_2-saturated 0.1 M KOH solution at various rotation speed: (a) Fe/P-C-700, (b) Fe/P-C-800, (c) Fe/P-C-900, (d) Fe/P-C-1000, (a) Fe NPs/P-C-1000, and (f) 20% Pt/C.

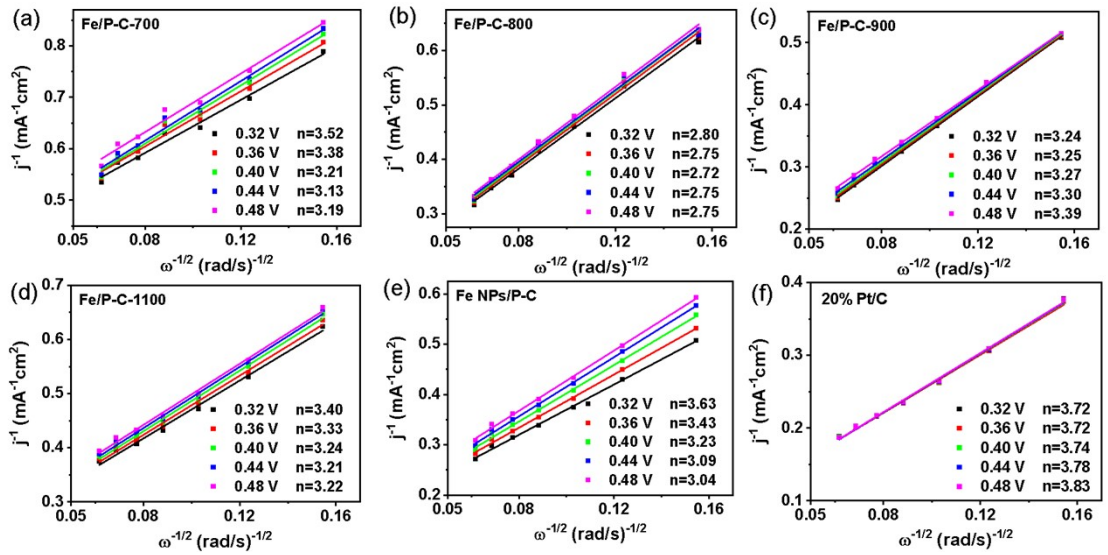

Figure S3. Koutecký-Levich plots of catalysts for the oxygen reduction reaction (ORR). Measurements were performed at various rotation rates, and the calculated electron transfer numbers (n) are shown for each corresponding current density: (a) Fe/P-C-700, (b) Fe/P-C-800, (c) Fe/P-C-900, (d) Fe/P-C-1000, (a) Fe NPs/P-C-1000, and (f) 20% Pt/C.

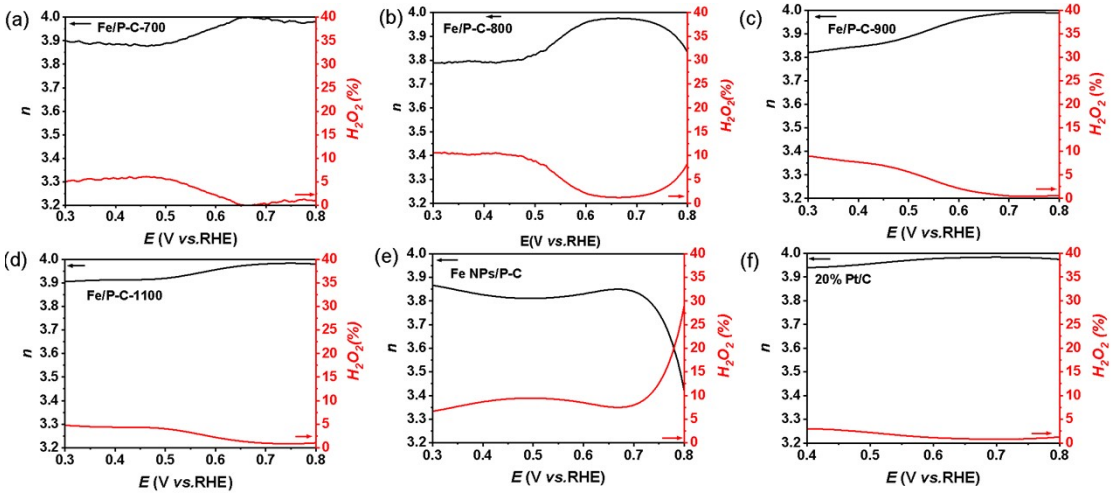

Figure S4. Comparison of H_2O_2 selectivity (percentage) as a function of applied potential (V vs. RHE) for different catalysts: (a) Fe/P-C-700, (b) Fe/P-C-800, (c) Fe/P-C-900, (d) Fe/P-C-1000, (a) Fe NPs/P-C-1000, and (f) 20% Pt/C.

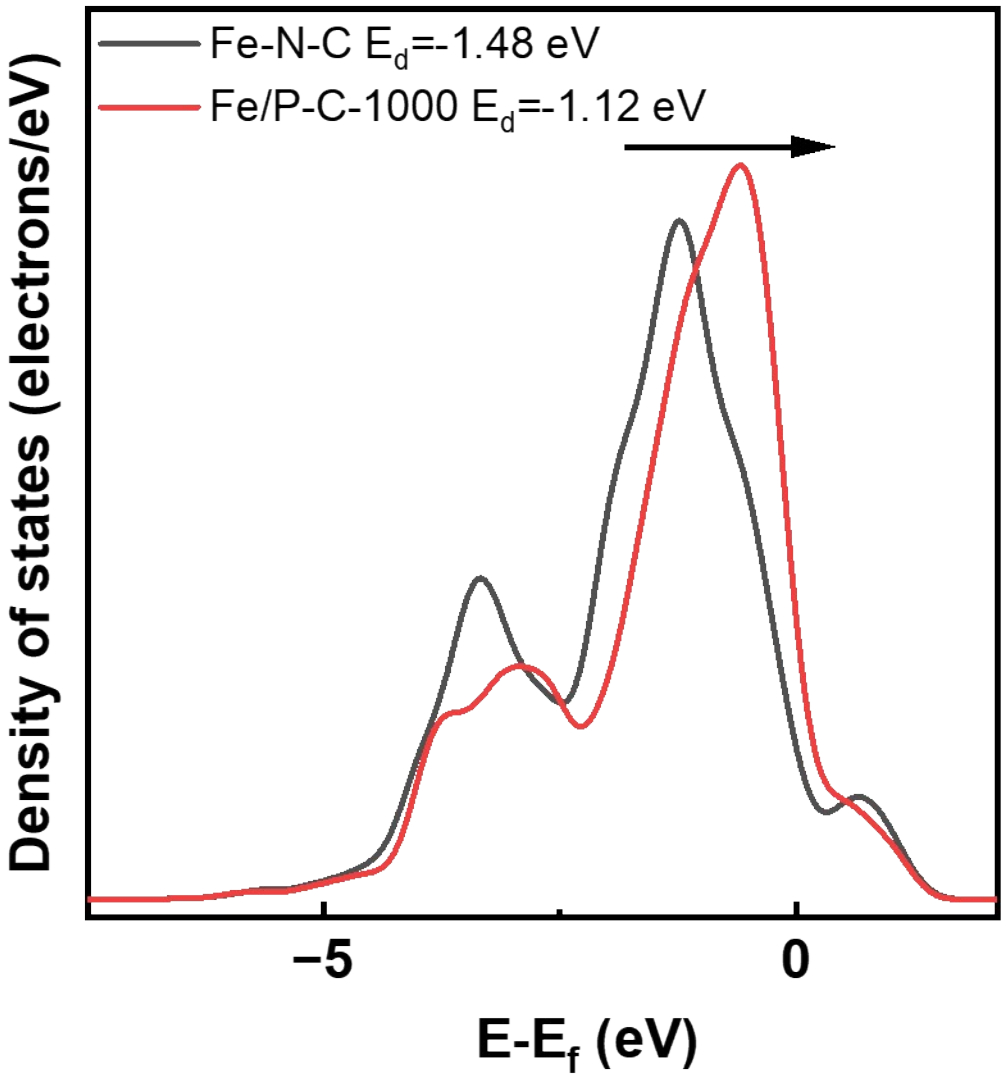

Figure S5. Density of states (DOS) calculated by DFT for Fe-based catalytic models with and without phosphorus-induced electronic coupling.