# Supplementary Information

# Synergistic coupling of defective SO$_x$-containing carbon and iron phthalocyanine for efficient oxygen reduction

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## Experimental section

### 2.1. Chemical and reagents

Ammonium sulfate, ammonium chloride and iron phthalocyanine were purchased from Shanghai Macklin Biochemical Company Limited, while pyrrole was sourced from Shanghai Titan Scientific Company Limited. All reagents used were of

analytical grade and were employed without further purification.

## 2.2. Preparation process of the electrocatalysts

(1) Synthesis of polypyrrole (PPY) Precursors

A solution of 5.216 g ammonium sulfate in 16 mL of water (solution A) was combined with 1.6 mL of pyrrole dissolved in 16 mL of ethanol (solution B). The mixtures were vigorously shaken and allowed to react at 4 °C for 2 hours. The resulting PPY was washed and freeze-dried for collection.

(2) Synthesis of DSNC Precursors

In subsequent reactions, 6 g of $NH_4Cl$ and 0.250 g of PPY were placed in separate quartz boats and placed upstream and downstream, respectively, in a tube furnace. Pyrolysis was performed in an argon atmosphere at 900 °C for 2 hours with a heating rate of 10 °C per minute. SNC was synthesized using a similar method without adding $NH_4Cl$.

(3) Synthesis of U-DSNC

0.005 g of DSNC was dispersed in 120 mL of DMF solvent and sonicated for 2 hours. The resulting product was washed, centrifuged, and freeze-dried.

(4) Synthesis of FePc@DSNC

Firstly, 0.001 g of iron phthalocyanine (FePc) was dissolved in 50 mL of DMF to form a uniform solution (Solution A). Separately, 0.005 g of DSNC in 70 mL of DMF stirring dissolved to create another homogeneous solution (solution B). Solution A was then added to solution B and stirred for 2 hours. Finally, the product was washed, centrifuged, and freeze-dried.

(5) Synthesis of U-FePc@DSNC

0.001 g of FePc was dissolved in 120 mL of DMF by means of sonication. Subsequently, 0.005 g of DSNC was added in the above solution. After sonicating for 2 hours to make FePc molecules couple with carbon in DSNC via π–π interactions, the U-FePc@DSNC product was washed with DMF and deionized water, centrifuged, and freeze-dried. U-FePc@SNC was synthesized in a similar procedure, substituting DSNC with SNC.

## 2.3. Structure Characterization

XRD measurement was conducted on the X' Pert3 Powder assembled with Cu Ka radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) images were taken on Hitachi/SU8010, while transmission electron microscopy (TEM) images were obtained using Talos F200x equipped with an energy-dispersive X-ray spectroscopy analyzer. Aberration-corrected high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were captured on Titan Themis 60-300. Powder X-ray photoelectron spectroscopy (XPS) analysis was carried out using ESCALAB250Xi. Ultraviolet–visible (UV-vis) absorption spectra were measured on Agilent Technologies Cary 100 UV-Vis spectrophotometer.

## 2.4. Electrochemical Measurements

All electrochemical measurements are carried out in a three-electrode configuration based on the CHI660E workstation. The rotating disk or rotating ring disk glassy carbon electrode was used as the working electrode, the saturated calomel electrode (SCE) electrode and the graphite rod were used as the reference electrode and the counter electrode, respectively. To prepare the working electrode, 2 mg catalysts and 1 mg carbon powder (Vulcan XC-72) were dispersed into the mixture of 150 μL ethanol, 150 μL water and 10 μL Nafion under ultrasonication for 60 min to form the uniform ink. After that, 26 μL of the prepared ink was dropped on the working electrode and dried naturally. 0.1 M KOH electrolyte was bubbled with $O_2$ or $N_2$ for 30 min before the measurement.

The electron transfer number (n) is calculated by the K-L equation as follows.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K}$$

$$B = 0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

where J is the measured current density and $J_L$ is the diffusion-limiting current density, ω is the angular velocity of the disk (=2πr/60, r is the rotation speed in round/min), n

is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (96485 C mol$^{-1}$), $C_0$ is the bulk concentration of O$_2$ (1.2×10$^{-6}$ mol cm$^{-3}$), $D_0$ is the diffusion coefficient of O$_2$ (1.9×10$^{-5}$ cm$^2$ s$^{-1}$), and V is the kinematic viscosity of the electrolyte (0.01 cm$^2$ s$^{-1}$).

The electron transfer number (n) and hydrogen peroxide yield (H$_2$O$_2$%) of the material were measured by rotating disk-electrode (RRDE). The calculation method is as follows.

$$H_2O_2\% = 200 \times \frac{\dfrac{I_R}{N}}{I_D + \dfrac{I_R}{N}}$$

$$n = 4 \times \frac{I_D}{I_D + \dfrac{I_R}{N}}$$

where $I_D$ is the disk current, $I_R$ is the ring current, and N (0.37) is the ring collection efficiency.

## 2.5. ZAB assembling

The homemade ZAB was used to measure the Zn-air battery. In order to prepare the air cathode, the as-prepared ink was evenly coated on the carbon paper with a gas diffusion layer, and drying at 60 °C. The catalyst loading was 1.2 mg cm$^{-2}$. A polished Zn plate (thickness of 1.5 mm) was used as the anode. 6 M KOH aqueous was used as the electrolyte. The test is executed at room temperature.

## 2.6. Computed methods

DFT calculations were performed using Vienna abinitio simulation package (VASP) employing the projector-augmented wave (PAW) method.[1] The exchange-correlation function was calculated using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) implementation.[2] A plane wave expansion with cut-off energy of 450 eV was used for all calculations. K-points sampling with a Monkhorst-Pack mesh scheme was set as 3×3×1 for structural relaxation in adsorption energies until the energies were less than 1×10$^{-4}$eV and the

absolute value of the Hellmann-Feynman force less than 0.01 eV Å⁻¹. A vacuum region with a thickness of 15 Å was constructed in the z direction to minimize the interaction between adjacent image cells. In structural relaxation, all atoms are allowed to relax.

The following equation is used to calculate the Gibbs free energy of each elementary step.

$$\Delta G = \Delta E + \Delta ZPE - T * \Delta S + ne * U$$

where $\Delta E$ is the reaction energy calculated by DFT. $\Delta ZPE$ and $\Delta S$ are the correction of zero-point energy and the variation of entropy, respectively. $T$ is the temperature (T = 298.15 K). $ne$ and $U$ are the number of transferred electrons and the bias voltage applied on the electrode, respectively.

The four elementary steps of ORR are defined as ΔGi (i=1−4) The overpotential of ORR (η ORR) can be written as

$$\eta\,ORR = \frac{\max\{\Delta G1,\,\Delta G2,\,\Delta G3,\Delta G4\}}{e} + 1.23$$
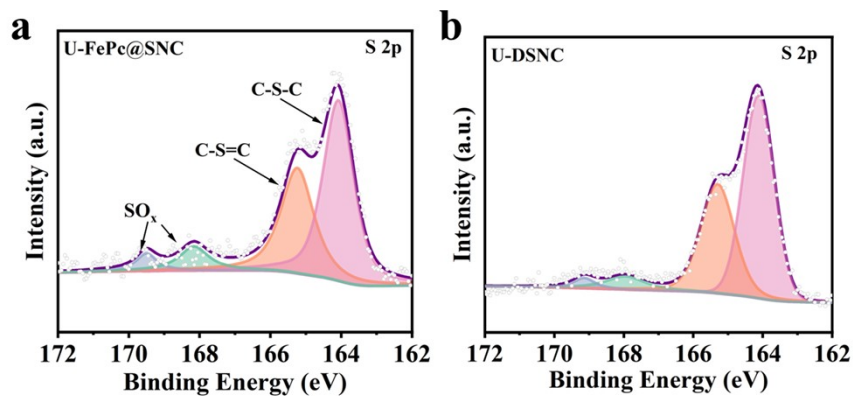


**Fig. S1** High-resolution S 2p XPS spectra of (a) U-FePc@SNC and (b) U-DSNC.
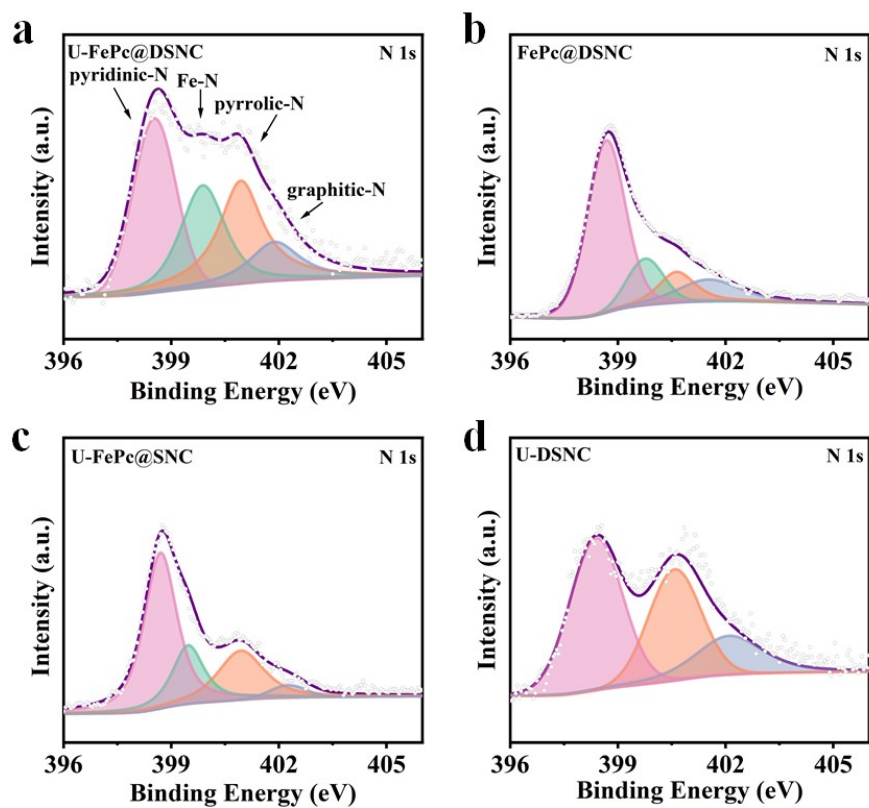
**Fig. S2** High-resolution XPS N 1s spectra of (a) U-FePc@DSNC, (b) FePc@DSNC, (c) U-FePc@SNC and (d) U-DSNC.
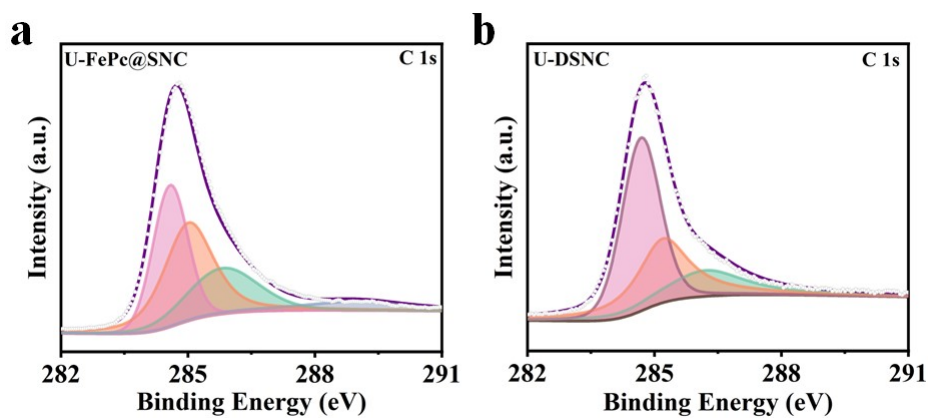


**Fig. S3** High-resolution XPS C 1s spectra of (a) U-FePc@SNC and (b) U-DSNC.
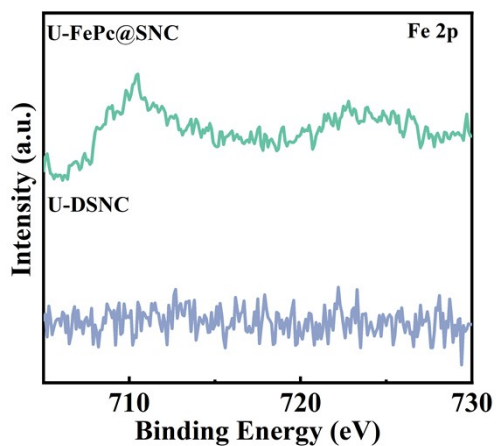
**Fig. S4** High-resolution XPS Fe 2p spectra of U-FePc@SNC and U-DSNC.
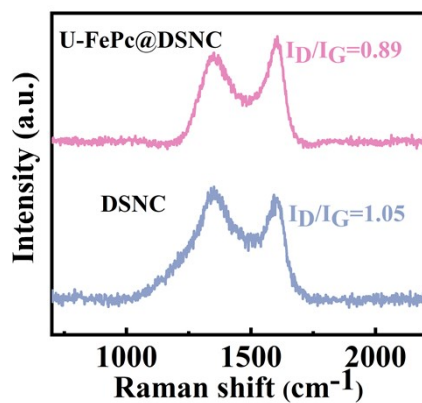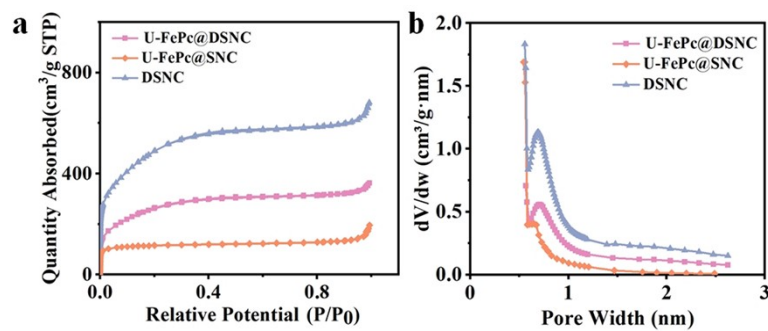


**Fig. S5** Raman spectra of U-FePc@DSNC and DSNC.



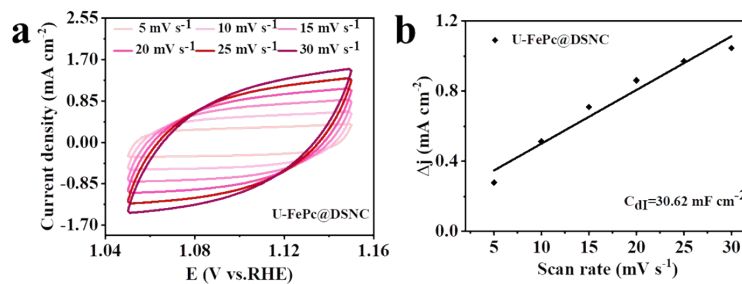**Fig. S6** (a) $N_2$ adsorption–desorption isotherms and (b) pore size distribution plots of U-FePc@DSNC, U-FePc@SNC and DSNC.

**Fig. S7** (a) CV curves at different scan rates and (b) Electrochemical active surface area (ECSA) of U-FePc@DSNC.
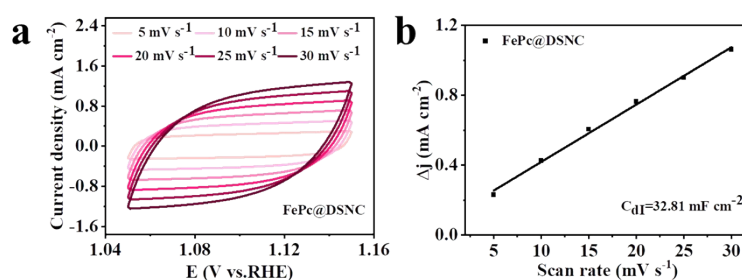


**Fig. S8** (a) CV curves at different scan rates and (b) ECSA of FePc@DSNC.
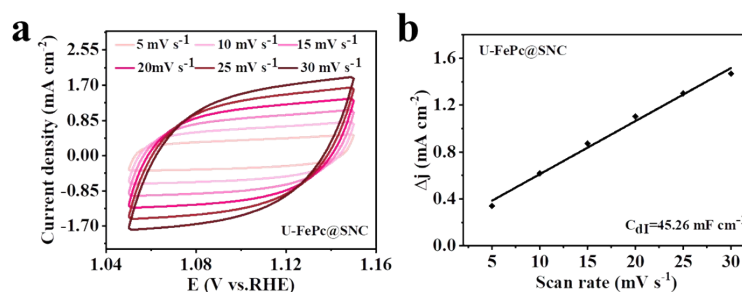


**Fig. S9** (a) CV curves at different scan rates and (b) ECSA of U-FePc@SNC.
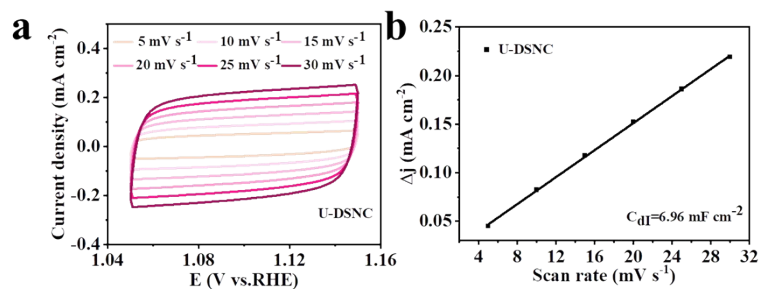


**Fig. S10** (a) CV curves at different scan rates and (b) ECSA of U-DSNC.
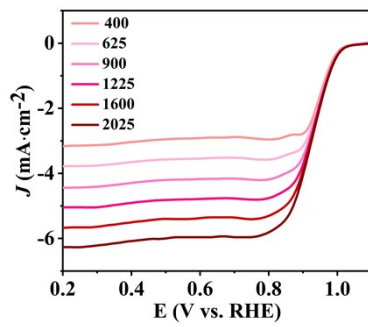
**Fig. S11** LSV curves at different rotation speeds.



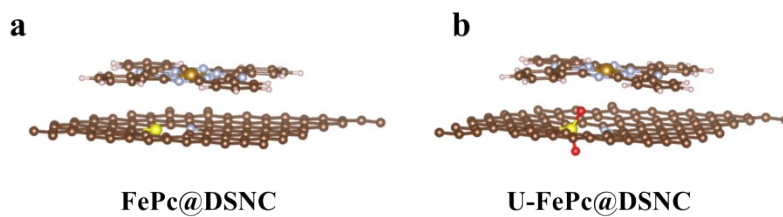**Fig. S12** Differential charge density of FePc@DSNC (lift) and U-FePc@DSNC (right)



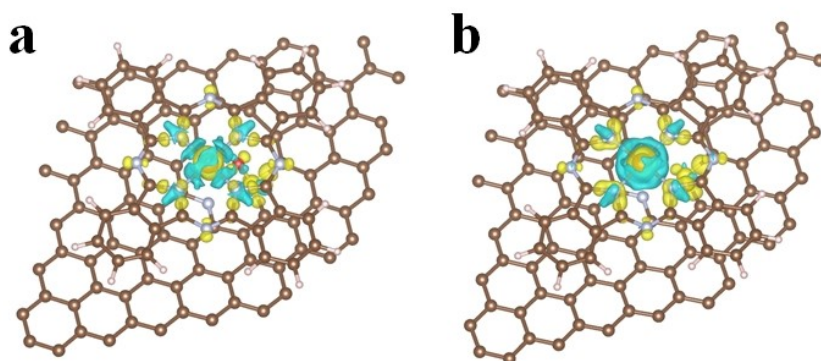**Fig. S13** Calculation model of (a) FePc@DSNC and (b) U-FePc@DSNC.



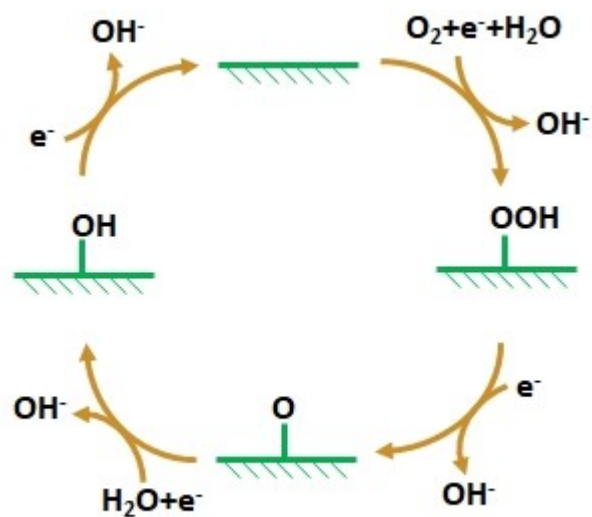**Fig. S14** Differential charge density of (a) U-FePc@DSNC and (b) FePc@DSNC.
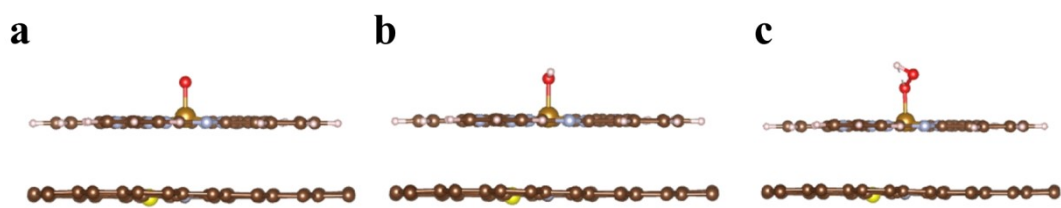
**Fig. S15** ORR four-electron reaction pathway.

a            b            c



**Fig. S16** Structure of FePc@DSNC after adsorption of (a) O*, (b) OH* and (c) OOH*.
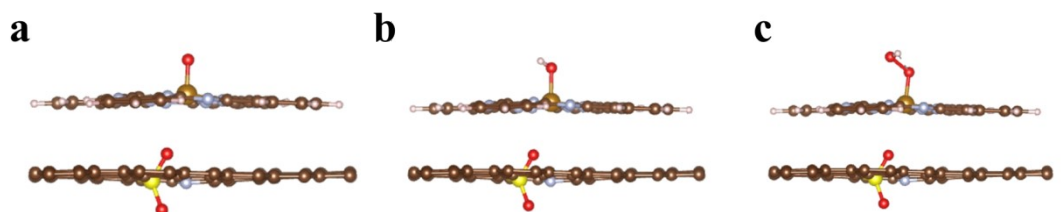
a            b            c



**Fig. S17** Structure of U-FePc@DSNC after adsorption of (a) O*, (b) OH* and (c) OOH*.
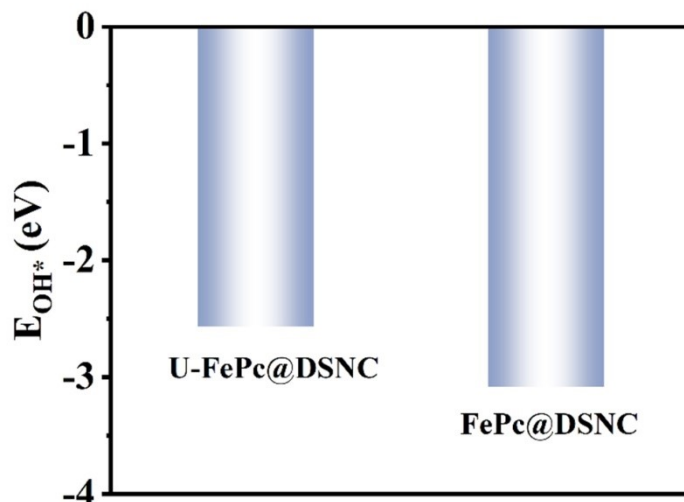
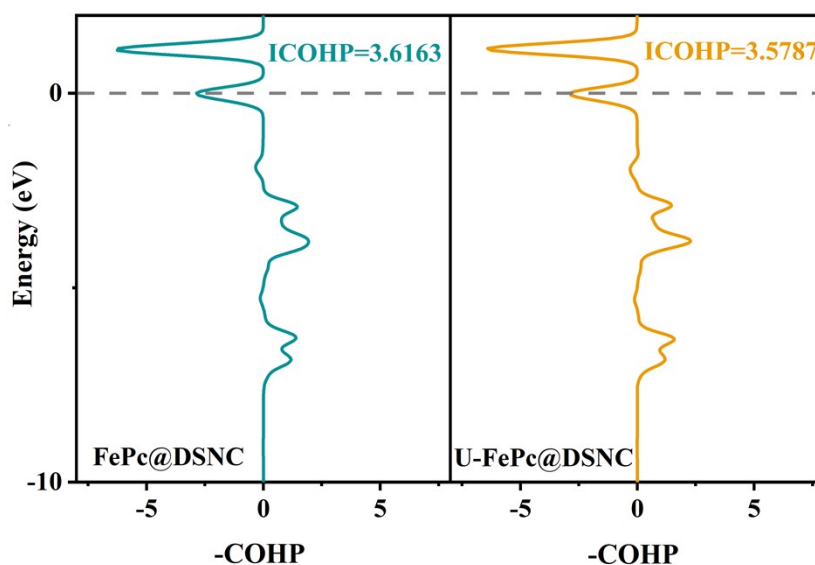**Fig. S18** OH* adsorption energy of U-FePc@DSNC and FePc@DSNC.



**Fig. S19** The COHP analysis of HO-FePc@DSNC and HO-U-FePc@DSNC for Fe-O.

## References:

(1) Kresse, G.; Hafner, J. Ab initiomolecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium. *Physical Review B* **1994**, *49* (20), 14251–14269.

(2) John P. Perdew; Kieron Burke; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.