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Substituent-modulation induced electronic perturbations can fine-tune the charge cloud distribution around carbon defects. The transfer of electrons from electron-donating substituents to carbon defects will lead to lower p_z band center of carbon atoms, stronger C–O bonds, narrower band gaps, and asymmetric orbital distribution, consequently enhancing the ORR thermodynamic activity and kinetic efficiency.

Due to their flexible physical structures, high electronic conductivity, excellent chemical tolerance, and tunable charge distribution, carbon-based electrocatalysts, which have been considered as highly promising candidates to replace expensive and scarce Pt-based catalysts in fuel cells, have garnered significant research attention.^{1–4} Various types of carbon-based electrocatalysts such as heteroatom doped carbon and topologically defective carbon have demonstrated exceptional ORR performance.^{5–8} For example, Wu *et al.* recently reported a high-density carbon defect catalyst with a competitive half-wave potential of 0.90 V (vs. RHE, in 0.1 M KOH).⁹ Furthermore, experiments successfully demonstrated that edge-located carbon defects serve as the genuine active centers, while heteroatoms merely play a role in the fine-tuning of the electron cloud around the carbon defects.¹⁰

Upon delving into more theoretical insights, the three sp^2 orbitals of adjacent carbon (C) atoms form stable σ bonds

Enhanced ORR activity of carbon defects *via* substituent-modulated electronic perturbation†

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through a head-to-head framework.¹¹ Meanwhile, the unhybridized p_z orbitals perpendicular to the σ bond form side-by-side π bonds. The σ and π bonds together form a stable inert carbon ring.^{11–13} When adsorbing ORR intermediates, *i.e.* OOH, O, and OH groups, the formation of C–O bonds primarily relies on the charge transfer between the p_z orbital of C and the p orbital of O.^{14,15} The presence of carbon defects can activate the inert p_z orbital of C, thereby enhancing the adsorption ability of oxygen groups.^{16,17} However, according to the Sabatier principle, a moderate adsorption energy is critical to high catalytic activity.¹⁸ Consequently, a meticulous fine-tuning of the electron distribution in the p_z orbital of carbon can lead to the peak ORR catalytic activity on defective carbons.

Recently, a novel approach has emerged for fine-tuning the electron structure of the active center by electronic perturbation from adjacent functional groups. Shao *et al.* fabricated a series of functionalized Fe-phthalocyanine-based catalysts (FePPc-R/C) and got a 20-fold enhancement in mass ORR activity.¹⁹ Duan *et al.* employed functional groups to adjust the charge distribution around the Cu active center in graphdiyne-based (G DY) single-atom catalysts (SACs), achieving an optimal faradaic efficiency of 72.3% for producing CH₄ over Cu SAC supported on the F-substituted G DY.²⁰ Mao *et al.* revealed that COOH-decorated MIL-53 (Cu) achieved a high faradaic efficiency of 55.5% in the reduction of CO₂ to CH₃CH₂OH through a combined theoretical and experimental study.²¹ Meanwhile, carbon defects with specific functional groups can be easily synthesized, and the types of substituents are, to some extent, controllable.^{22,23} Therefore, fine-tuning the p_z orbitals of carbon defects through substituent functionalization stands out as a viable and promising strategy, but has not been reported yet.

With the aim of systematic modulation of the electronic structures of carbon defects, we proposed to tailor the 585 defects (composed of two pentagons and one octagon) by introducing electron-withdrawing (–NO₂, –CF₃, –COOH, and –SO₃H) and electron-donating groups (–CH₃, OCH₃, –NH₂, and –NHCH₃). The designed catalysts were named as 585-R (here R represents functional groups). Our DFT calculations reveal that carbon

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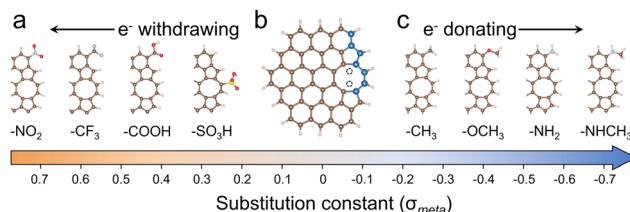


Fig. 1 The structures of the pristine and substituent functionalized 585 defects: (a) 585 defects with electron withdrawing functional groups, (b) pristine 585 defects, and (c) 585 defects with electron donating functional groups.

defects decorated with electron-donating groups exhibited down-shifting p_z orbitals, resulting in stronger C–O bonds and superior ORR activity compared to pristine carbon defects. For instance, 585–NHCH₃ showed an ORR overpotential of 0.53 V. In contrast, electron-withdrawing substituents increased the p_z band center, impeding the ORR activity over carbon defects. Additionally, the substituent constant of the functional groups is proved to be an effective descriptor for predicting the electronic structure and ORR activity of substituent-decorated carbon defects.

A carbon cluster model containing an edge-located 585 defect was built by removing two carbon atoms based on previous experimental and theoretical investigations (marked as black dashed circles in Fig. 1b).^{5,24} Seven edge carbon atoms, highlighted as blue color in Fig. 1b, were selected to be potential active sites to evaluate the ORR activity. Furthermore, as schematically illustrated in Fig. 1, we select the eight types of substituents with a decreasing substituent constant (σ_{meta}), ranging from electron-withdrawing groups to electron-donating groups (Table S1, ESI[†]).^{25,26} These functional groups will be used to substitute the –H protons near or in the 585 defects, leading to substituent functionalized defective carbon electrocatalysts (FDCs). Meanwhile, three substitution sites (sites 1, 2, and 3) were chosen in terms of symmetry of the carbon cluster models, and a total of 24 FDCs were constructed to test their ORR activity (Fig. S1, ESI[†]). Fig. 1a and c illustrate the optimized substituted structures with the highest ORR activity for each functional group. Note all the chosen functional groups substituted at site 1 exhibit the highest ORR activity, except for –SO₃H, which is located on site 3.

Subsequently, the ORR activities on all the 25 models including 24 types of FDCs and pristine 585 defect were calculated, and the results are listed in Fig. S2, S3 and Tables S2–S10 (ESI[†]). Fig. 2a and b depict the optimal ORR energy pathways of 585 defects with and without the functional group. Apparently, the decoration of an electron-withdrawing substituent results in lower ORR activity than that of the pristine 585 defect. The theoretical ORR overpotential (η_{ORR}) of 585–NO₂ is 0.78 V, which is 0.26 V higher than that of the pristine 585 defect. In contrast, the functionalization of electron-donating groups can significantly promote the ORR activity on 585 defects, with 585–NHCH₃ exhibiting the lowest η_{ORR} of 0.53 V. The potential determining step (PDS) of all the nine kinds of designed electrocatalysts is the hydrogenation of O₂, *i.e.*, O₂ → *OOH. The adsorption energies of the ORR reaction intermediates on

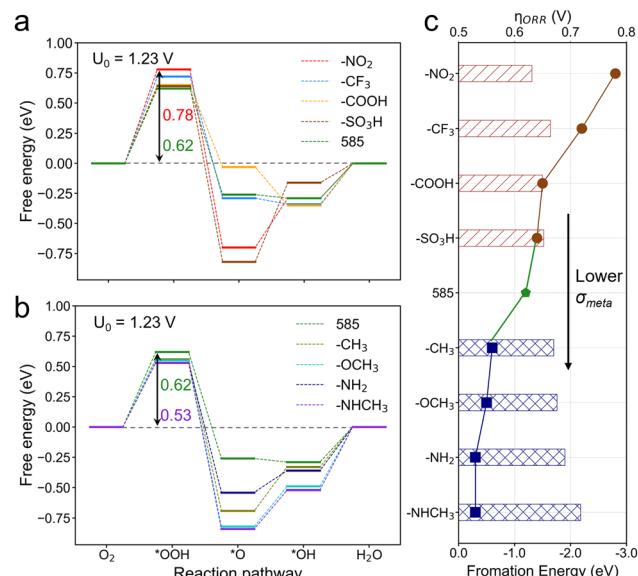


Fig. 2 The optimal ORR energy profiles of (a) electron-withdrawing group and (b) electron-donating group functionalized 585 defects. (c) The formation energies of substituent functionalized 585 defects and the corresponding η_{ORR} . The functional groups are listed from top to bottom with decreasing σ_{meta} .

the functionalized carbon defects demonstrated linear scaling relationships, as shown in Fig. S4 (ESI[†]). The adsorption energy of the OOH group ($\Delta E_{ads}(\text{OOH})$) is deemed to be a good descriptor for describing ORR activity on the FDCs. The FDCs exhibit the highest ORR activity at $\Delta E_{ads}(\text{OOH})$ around 3.88 eV. As the interaction of a material with external environmental agents largely depends on its intrinsic stability, the stability of functionalized 585 defects can be quantitatively described by their formation energy, defined as the binding energy of substituents and defects (eqn (S11) in ESI[†]). As shown in Fig. 2c and Fig. S5 (ESI[†]), the substituent functionalizations on 585 defects are all exothermic, indicating the high stability of the designed electrocatalysts.

The introduction of different substituents into carbon defects can substantially modulate the electronic structure and the physical environment of the active sites. Thus, based on the aforementioned eight types of FDCs with optimal ORR activity, the charge redistribution around the 585 defects was thoroughly investigated. Firstly, differential charge distribution and Bader charge analysis were performed to examine the electron transfer between substituents and carbon defects. Fig. 3a and Fig. S6 (ESI[†]) present the plot of charge difference of the FDCs. It can be clearly seen that carbon atoms near the electron-withdrawing substituents show electron-depletion, whereas the electron-donating substituents lead to charge-accumulation around the defects. Then, Bader charge analysis was conducted to quantitatively evaluate the volume of charge translation from carbon defects to substituents (CT) (as shown in Fig. 3b and Fig. S7, S8, ESI[†]). It was found that there will be 0.35 |e| of electrons transferring from carbon defects to electron-withdrawing substituents, while electron-donating substituents will donate as much as 0.19 |e| electrons to carbon defects.

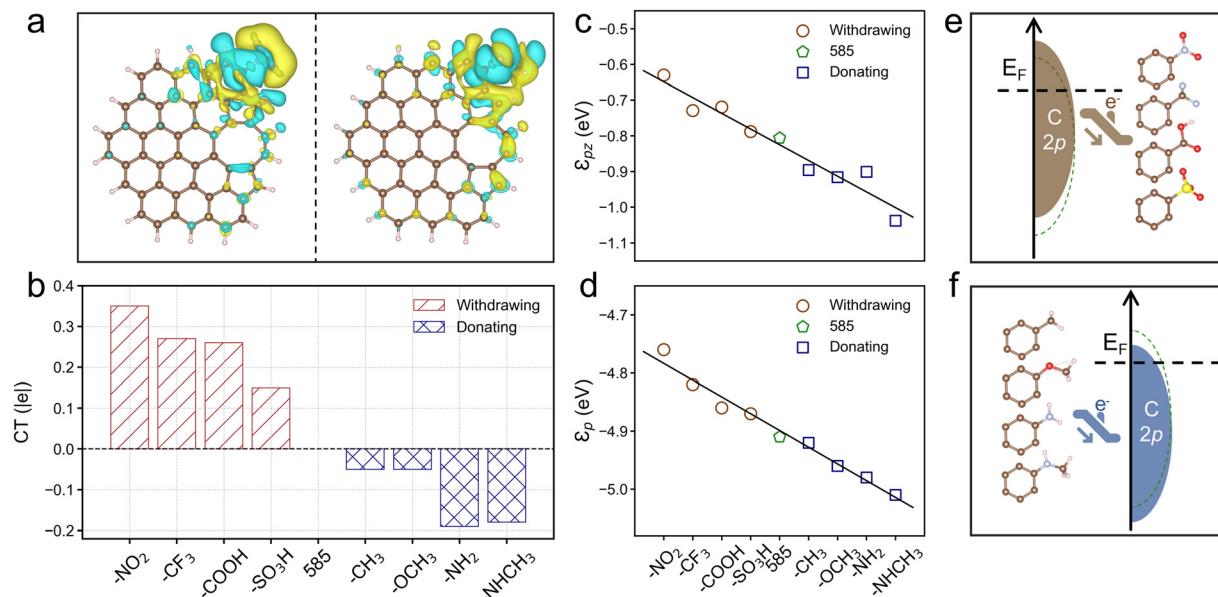


Fig. 3 (a) Differential charge density distributions of (left) 585-NO₂ and (right) 585-NHCH₃. The yellow and blue colors represent electron accumulation and depletion regions, respectively. The isosurface value is $3 \times 10^{-4} \text{ e } \text{\AA}^{-3}$. (b) The volume of charge transfer from carbon defects to substituents (CT). The p_z band center (c) and p band center (d) of FDCs. Schematic diagram of electron redistribution of FDCs caused by substituent functionalization: (e) electron-withdrawing substituents and (f) electron-donating substituents.

Previous studies have demonstrated that the unfulfilled p_z orbitals (π bonds), perpendicular to the σ bond plane, serve as the primary electronic acceptors or donors in the carbon ring.³ Then, the PDOS of the p_z orbital of carbon atoms in FDCs are calculated, as displayed in Fig. S9a and b (ESI[†]). Meanwhile, the p_z-band centers (ε_{p_z}) were calculated, showing a decreased tendency (from -0.63 to -1.04 eV, Fig. 3c), as well as their p-band centers (ε_p , from -4.76 to -5.01 eV, Fig. 3d and Fig. S10, ESI[†]) when the substituents are changing from electron-withdrawing to donating. So, the functional groups can significantly tune the electronic structure and electron amounts in the p orbital of carbon atoms, especially the p_z orbital and π bonds in the carbon rings, as shown in Fig. S11 (ESI[†]) and Fig. 3e, f, thus modulating their adsorption capacity of reaction intermediates and ORR catalytic activity. Furthermore, the introduction of substituents can induce narrower band gap and non-uniform charge distribution, enabling the carbon defects to possess higher dipole moment to facilitate the electron transfer from the HOMOs to the O₂ molecule (Fig. S12–S14, ESI[†]). Above all, the electronic perturbation through the substituent functionalization can substantially enhance the ORR performance of carbon defects both thermodynamically and kinetically.

The charge transfer between carbon defects and functional groups is responsible for the fluctuation of η_{ORR} . The pK_a, *i.e.* negative natural logarithm of acid dissociation constant of these electrocatalysts should directly be proportional to the standard Gibbs free energy change of the ORR. As substituents are here mainly used to tune the electronic properties of FDCs, a reasonable hypothesis emerged: there should be a potential correlation between the pK_a value of the functional group and the catalytic activity of the catalyst. However, determining the pK_a value is challenging due to its dependence on multiple

factors. Fortunately, substituent constants (σ_{meta}) of the substituents are known and represented by the following equation:²⁵

$$\sigma_{\text{meta}} = \log(K_{\text{a}}(R)/K_{\text{a}}(\text{H})) \quad (1)$$

where, $K_{\text{a}}(R)$ and $K_{\text{a}}(\text{H})$ are the acid dissociation constant of the substitution group and H, respectively. σ_{meta} can quantitatively describe the electronic effect of a functional group, with the value being positive, negative or zero depending on whether the substituent is an electron acceptor or electron donor.

As mentioned earlier, eight substituents in this work were chosen according to their decreasing σ_{meta} . Firstly, in Fig. 2c, we can find that substituents with lower substituent constant can enable carbon defects with a lower ORR overpotential. Moreover, a liner relationship between η_{ORR} and σ_{meta} can be fitted as $\eta_{\text{ORR}} = 0.614 + 0.154 \sigma_{\text{meta}}$ ($R^2 = 0.88$, Fig. S15, ESI[†]). Furthermore, the charge redistribution and modification of the electronic structure of FDCs during the substituent functionalization are closely related to the substituent constants (see Fig. 4). Consequently, all these scaling relationships suggest that the substituent constant can be a good descriptor to accurately predict the ORR efficiency of the designed electrocatalysts.

In summary, we report that electron-donating substituents can transfer small amounts of electrons to carbon defects, leading to non-uniform charge distribution around carbon defects, an asymmetric molecular framework, and narrow band gaps, as well as low p and p_z band center of carbon atoms. The introduction of electron-donating substituents can enhance the ORR activity of carbon defects, with 585-NHCH₃ exhibiting superior performance with an ORR overpotential of 0.53 V only. In contrast, the functionalization of electron-withdrawing substituents increases the bandgap, and moves the p band center

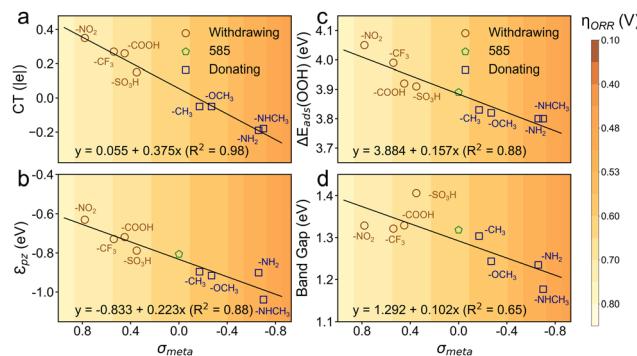


Fig. 4 The linear relationships between σ_{meta} and (a) charge transfer between substituents and carbon defects (CT), (b) p_z band center of carbon atoms in FDCs (E_{p_z}), (c) the adsorption energies of OOH groups ($\Delta E_{ads}(OOH)$), and (d) calculated band gaps of FDCs. The contour background represents η_{ORR} with σ_{meta} as a descriptor.

to higher energy levels, thus weakening the C–O bonds in reaction intermediates to impede the ORR activity of carbon defects. For example, 585- NO_2 displays an ORR overpotential of 0.78 V, which is 0.26 V higher than that of the pristine 585 defect. Importantly, we discovered that substituent constants of the substituents (σ_{meta}) can serve as a reliable descriptor for predicting the electronic structure and ORR activity of defective carbons. Functional groups with lower σ_{meta} values are associated with higher ORR activity in defective carbons. Our work highlights a novel approach to enhance the ORR activity of defective carbon-based electrocatalysts, opening new possibilities for the development of high-performance metal-free ORR catalysts.

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Data availability

The data supporting this article has been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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