Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) have been widely studied due to their extensive applications in energy conversion and storage.[1–10] However, the complicated multielectron transfer processes and high energy barrier of activating reactant lead to a high overpotential that could influence the catalytic performance.[31,32] Therefore, in order to overcome high catalytic reaction barrier, designing the hybrids of the TMPs and defective carbon and probing the interfacial charge distribution behavior are highly desirable to realize bifunctional oxygen electrocatalysis.

Herein, we constructed a new type of hybrids of the CoP and defective carbon (marked as CoP–DC). We revealed the interfacial charge transfer process of the hybrids by multiple synchrotron-based X-ray absorption structure, ultraviolet photoelectron spectra (UPS), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. The interfacial charge redistribution was observed, which subsequently contributed to enhanced ORR activity on the defective carbon and enhanced OER activity on the CoP.

The CoP–DC hybrids were synthesized through a simple phosphorization reaction toward the CoOx-contained polymer hydrogel. Typically, the polymer hydrogel was obtained by inserting CoOx-into polymer hydrogel framework under alkaline condition according to previous reports, and then was phosphorized...
by nontoxic red phosphorus under N₂ flow at 900 °C (see Supporting Information for details). For comparison, the DC and the Co nanoparticles-contained DC (Co–DC) were also obtained under the similar condition without the addition of Co ion and red phosphorus, respectively. X-ray diffraction (XRD) was carried out to investigate the crystal structure of CoP–DC and the control samples. As shown in Figure 1a, XRD pattern of the DC sample shows wide peak at 26°, suggesting the typical defective structure with low long-range order. The metallic Co peaks for Co–DC at 44° and 51°, indicating that the Co ion has been reduced to metallic Co during the anneal process under N₂ flow at 900 °C. For the CoP–DC, a series peaks at 31.6°, 35.3°, 36.3°, 46.2°, 48.1°, 52.3°, and 56.0° can be assigned to the (011), (200), (111), (211), (103), and (301) lattice planes of CoP (JCPDS: 29–0497), respectively, indicating the CoP component inside the obtained samples. The Raman spectra (Figure S1, Supporting Information) of CoP–DC and DC show two dominant peaks at 1340 and 1590 cm⁻¹ corresponding to the D and G band, respectively. Comparing to that of pure DC, the intensity ratio (I_D/I_G) of D and G band decreased in CoP–DC and Co–DC samples due to the graphitization during anneal process, implying the well interfacial contact between the CoP or Co nanoparticles and DC. Co–DC exhibited the lowest I_D/I_G ratio indicating the much lower defects density in Co–DC.[33,34] To further probe the microstructure, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of CoP–DC were performed, showing that the CoP nanoparticles (average diameter of 30 nm) were uniformly embedded into the DC to form core–shell structure (Figure 1b,c). Besides, CoP nanoparticles in CoP–DC show the similar sizes comparing to Co nanoparticles in Co–DC (Figure S2a, Supporting Information), which means that the phosphorization had no influence on the size of nanoparticles during the anneal process (Figure S2b,c, Supporting Information). Furthermore, the CoP nanoparticles in the CoP–DC show continuous and ordered lattice fringes with the lattice spacings of 2.47 and 3.75 Å and the crystal plane angle of 86.4° (Figure S3, Supporting Information), which correspond to the (11T) and (101) planes, respectively, according to the lattice parameters of the CoP (JCPDS 29–0497). Notably, the carbon layers around the CoP exhibit typical curved lattice fringes, revealing the defective structure. Thermogravimetric analysis (TGA) of CoP–DC and HNO₃-treated CoP–DC (see Supporting Information for details) were conducted to explore the defective features. The mass fraction of CoP nanoparticles in DC–CoP was calculated to be 57.32%, while the value decreased to 11.42% in the HNO₃-treated CoP–DC, indicating that ≈80% of CoP nanoparticles in CoP–DC were not fully encased by the carbon. The above TEM observation and TGA results further reveal that the carbon layers exhibit abundant structural defects, displaying the typical interfacial structure with the exposure of dual components (As shown in Figure 1e, the dotted circle means the defective carbon sites).

To investigate the electronic structure of the CoP–DC, soft X-ray absorption near-edge structure (XANES) measurement was used to detect the L-edge excitation of elemental Co and K-edge excitation of elemental C (Figure 2a,b). As can be seen from Figure 2a, two separated peaks of Co L-edge XANES spectra at around 777 and 792 eV are assigned to the L₃ and L₂ edges of core electrons transition from 2p₃/2 and 2p₃/2 hybrid orbit to P 3p level, respectively. The different intensity of the absorption peaks is mainly caused by the different vacancies of unoccupied states of Co sites. Comparing to CoP bulk, the CoP–DC own stronger L₃ intensity, indicating that more vacancies existed in Co 3d states of CoP–DC, probably due to the electron transfer from the Co sites to C sites.[35,36] To further verify this, the C K-edge spectra was analyzed. From Figure 2b, the absorption peak A at 284 eV responds to π* structure and peak D at 291 eV responds to σ* structure of C–C bonds, respectively. In addition, we also observed

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**Figure 1.**

a) XRD of the CoP–DC and control samples. b) TEM and c) HRTEM images of the CoP–DC. d) TGA of CoP–DC sample and HNO₃-treated CoP–DC sample. e) Diagrammatic drawing of the morphology structure for the CoP–DC.
the peaks (marked as peak B) between $\pi^*$ and $\sigma^*$ owing to the sp$^3$ hybrid bonds between C and other functional-groups such as C=O and C–O (COOH). The DC sample shows the strongest peak B, indicating the most sp$^3$ hybrid bonds between C and other functional-groups than other samples. For the Co–DC and CoP–DC, the intensity of the peak B significantly decreased, which can be attributed to the catalytic graphitization of the Co and CoP during heating process. The intensity of peak B for the Co–DC is slightly weaker than that of CoP–DC, indicating that the less defects in the DC framework of Co–DC, which can be also observed from Raman spectra mentioned above. Notably, the intensity of peak A and D for the CoP–DC is the weakest, indicating the strongest electrons coupling and most electron transfer from the Co sites to C sites.[37,40,41] This result is in good agreement with XPS analysis (Figure S4, Supporting Information).

First-principles calculations (see the Supporting Information for details) were also performed to understand the interfacial charge redistribution on the CoP–DC interfacial structure. Differential charge density of the CoP–DC hybrids shows that electrons would migrate from CoP to DC layer due to the strong interfacial polarization between each other (Figure 3c). As a result, DC surface would collect electrons while CoP accumulate positive charges (holes), inducing the electron separation and hole distribution. Bader charge analysis further found that 1.30 electrons could gather at the outer DC surface. This electron accumulation would be beneficial to the following ORR on the defective carbon. Besides, it is well documented that the holes collection at the CoP could promote the formation of true catalytically active sites (CoOOH) for OER,[51,52] thereby boosting the OER performance. As such, the interfacial charge redistribution on the CoP–DC interfacial structure would simultaneously facilitate the ORR and OER.

In order to evaluate the expected bifunctional performance of the designed CoP–DC hybrids, both the ORR and OER measurements were carried on rotating disk electrode (RDE) and rotating RDE (RRDE) in 0.1 M KOH solution (Figure 4). Cyclic voltammetry (CV) curves for CoP–DC (Figure 4a) shows no featured peak for cathodic current in N$_2$-saturated KOH electrolyte within the potential range from −0.02 to 1.02 V (vs RHE), while an obvious oxygen reduction peak at 0.74 V, 0.95 V in O$_2$-saturated KOH electrolyte is presented, suggesting a distinct oxygen reduction activity for CoP–DC. Liner sweep voltammetry
(LSV) curves of all the as-prepared samples under rotating rates of 1600 rpm were further measured to compare the ORR performance (Figure 4b). Strikingly, CoP–DC shows the nearest onset potential comparing to commercial Pt/C and the half-wave potential (0.81 V vs RHE) is slightly lower than that of Pt/C (0.85 V vs RHE), indicating the excellent ORR performance of CoP–DC. The understanding of ORR mechanism is recorded from LSV curves under various rotation speed range from 225 to 2025 rpm with a scan rate of 10 mV s$^{-1}$ (Figures S7 and S8, Supporting Information). The $j_l$ increased with the rotating speed increasing owing to the shortened diffusion distance at high rotating speeds and enhanced mass transport at the electrode surface.$^{[51,54]}$ The Koutecky–Levich (K–L) plots express pretty good linearity and parallelism, indicating the first-order reaction kinetics toward the dissolved oxygen. Electron transfer number ($n$) and the formation of peroxide species (H$_2$O$_2^-$) were calculated from RRDE measurement at a rotation speed of 1600 rpm. The values of $n$ are 3.40, 3.45, 3.49, 3.80, and 3.82 for P–DC, DC, CoP bulk, Co–DC, and CoP–DC over a potential range from 0.2 to 0.8 V (vs RHE), respectively, and the percentage of peroxide species for CoP–DC is 16%, indicating a near four-electron ORR pathway in case of CoP–DC (Figure 4c; Figure S9, Supporting Information). Previous work verified that Co–N bond showed remarkable effect in ORR.$^{[55,56]}$ In order to eliminate the contribution of Co–N bonds which derived from the nitrogenous precursor (Figure S4d, Supporting Information), the CoP–DC was first dipped in 10 $\times$ 10$^{-3}$ M KSCN solution for 60 min to restrain the catalytic activity of Co–N species and then tested in 0.1 M KOH for ORR.$^{[55,56]}$ As shown in Figure S10 of the Supporting Information, LSV curves to estimate the reaction kinetics toward OER (Figure 4e). Impressively, the CoP–DC shows a smallest value of Tafel slope (32.5 mV dec$^{-1}$) among all the as-prepared samples and even better than that of IrO$_2$, which means CoP–DC performing a better electron transfer efficiency. Electrochemical active surface areas were further measured by CV testing at different scan rate from 20 to 120 mV s$^{-1}$ to deep understand the active surface area of these as-obtained catalysts (Figure S12, Supporting Information). The CoP–DC shows highest double-layer capacitance ($C_d$) of 26.98 mF cm$^{-2}$, indicating the largest active surface area, which offers more active sites during electrocatalytic process. Moreover, the CoP–DC also shows an ideal stability during the long time (20 h) test in 0.1 M KOH at a constant current density of 10 mA cm$^{-2}$ (Figure S13, Supporting Information). As discussed above, the high density of holes on the CoP nanoparticles is definitely beneficial to OER process. According to previous significant reports$^{[51,52]}$ O-doped CoP and carbon supported metal hydroxides, typical hole-doped catalysts, show significantly enhanced OER activities. In the two studies, DFT calculations and experimental results strongly indicate the promoted conversion from the metal phosphides or metal hydroxides to the related oxyhydroxides. The oxyhydroxides are generally considered as actually active sites for OER.$^{[61,62]}$ Thus, the high density of holes on the CoP nanoparticles would promote the generation of Co-based oxyhydroxides and thereby boost the activities. More importantly, the overall electrocatalytic activities of all the samples were investigated (Figure 4f) at the current density of 10 mA cm$^{-2}$ for OER and ~3 mA cm$^{-2}$ for ORR (Table S2, Supporting Information). Notably, a lowest oxygen electrode
activity (ΔE) of CoP–DC obtained 0.76 V, indicating that CoP–DC owns excellent bifunctional performance, which is comparable to the recent works (Table S3, Supporting Information).

When decorating DC with CoP nanoparticles, the redistributed electrons and holes result in the high density of electrons gathered on the surface of DC and high density of holes gathered on CoP nanoparticles. Previous studies had revealed that the brilliant ORR activity of carbon-based materials mainly contributed by the large surface area, multiple active sites and high reduction states. As discussed above, the excellent bifunctional electrical performance of CoP–DC hybrids primary caused by the following aspects: (1) DC, with large surface area, has provided multiple active sites that made contribution to molecule capture; (2) the hybrids demonstrated a lowest Φ after CoP embedded into DC framework, thus decreased the reaction energy barrier;[49,63] (3) interfacial polarized electrons accumulated at the surface of DC was supposed to enhance the ORR while the holes accumulated at the CoP nanoparticles was a key factor in OER; (4) high density of electrons and holes promoted the speed of immediate product rebuilt on the catalysts surface, leading to the enhanced electrocatalytic performance.[54,64]

In summary, we developed the hybrids of CoP and defective carbon for efficient bifunctional oxygen electrocatalysis. We provided complete evidence that the interfacial charge redistribution occurred at the interface of CoP and defective carbon. Electrochemical tests suggested that the CoP–DC hybrids exhibited better ORR and OER activities comparing to the single component, indicating the key roles of the interfacial charge redistribution. The hybrids here have the potential for the application to promote the development of related energy technologies and devices. More importantly, the concept demonstrated here calls for future efforts on interfacial engineering for electrocatalysts design.

Figure 4. a) CV curves of CoP–DC in N₂ and O₂ saturated 0.1 m KOH electrolyte. b) ORR LSV curves of as-prepared CoP–DC, Co–DC, DC, P–DC, and Pt/C in O₂-saturated 0.1 m KOH electrolyte at a rotation speed of 1600 rpm with a scan rate of 10 mV s⁻¹. c) Peroxide yield (black) and electron transfer number (n) (blue) of as-prepared CoP–DC, CoP bulk, Co–DC DC, and P–DC calculated from RRDE voltammograms. d) OER LSV curves and e) corresponding Tafel plots for CoP–DC, Co–DC, CoP bulk DC P–DC, and IrO₂. f) The overall LSV curves of all samples in the whole ORR and OER region in 0.1 m KOH.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrocatalysis, interfacial charges transfer, oxygen evolution reaction, oxygen reduction reaction, X-ray absorption spectra