One-Dimensional van der Waals Heterostructures as Efficient Metal-Free Oxygen Electrocatalysts

Chang Liu, Fei Liu, Hao Li, Junsheng Chen, Jingyuan Fei, Zixun Yu, Ziwen Yuan, Chaojun Wang, Huiling Zheng, Zongwen Liu, Meiying Xu, Graeme Henkelman, Li Wei, and Yuan Chen

ABSTRACT: Two-dimensional covalent organic frameworks (2D-COFs) may serve as an emerging family of catalysts with well-defined atomic structures. However, the severe stacking of 2D nanosheets and large intrinsic bandgaps significantly impair their catalytic performance. Here, we report coaxial one-dimensional van der Waals heterostructures (1D vdWHs) comprised of a carbon nanotube (CNT) core and a thickness tunable thienothiophene-pyrene COF shell using a solution-based in situ wrapping method. Density functional theory calculations and operando and ex situ spectroscopic analysis indicate that carbon–sulfur regions in thienothiophene groups in the COF serve as an active catalytic site for oxygen reduction and evolution reactions. The coaxial structure enables n-doping from the CNT core to the COF shell, which is controllable by varying COF shell thickness. The charge transfer from CNTs lowers COF’s bandgap and work function, which reduces the charge transfer barrier between the active catalytic sites and adsorbed oxygen intermediates, resulting in dramatically enhanced catalytic activity. The 1D vdWHs were applied as a bifunctional oxygen electrocatalyst in rechargeable zinc−air batteries, delivering a high speciﬁc capacity of 696 mAh gZn−1 under a high current density of 40 mA cm−2 and excellent cycling stability. The 1D vdWHs based on the coaxial structure of 2D COF wrapped around CNT cores may be further used as versatile building units to create multidimensional vdWHs for exploring fundamental physics and chemistry as well as practical applications in electrochemistry, electronics, photonics, and beyond.

KEYWORDS: covalent organic framework, carbon nanotube, van der Waals heterostructure, oxygen redox reaction, zinc-air battery

Two-dimensional covalent organic frameworks (2D-COFs) are planar nanosheets in a periodic lattice, assembled from covalently bonded small molecules. They possess several outstanding properties for enabling high-activity catalysts, for example, a large specific surface area, tunable porosity, and excellent thermal and chemical stability. More importantly, versatile molecular building blocks of 2D-COFs may offer well-defined and structurally tunable catalytic active sites with atomic precision. Recently, 2D-COFs have been explored as an emerging family of electrocatalysts for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The ORR and OER processes involve the transfer of four electrons. Their sluggish kinetics result in the unsatisfactory performance of many energy storage and conversion devices, such as zinc−air batteries (ZABs), fuel cells, and water electrolyzers. Precious metal based electrocatalysts, including platinum (Pt), ruthenium (Ru), and iridium (Ir), have high catalytic activity for ORR and OER; however, their high cost and low abundance on the earth limit their widespread applications. On the contrary, 2D-COFs can be synthesized at a low cost without using precious metals and may serve as efficient metal-free electrocatalysts for these electrochemical reactions. However, there are two challenges for these materials to serve as efficient electrocatalysts. First, abundant out-of-plane π-electrons on 2D-COFs cause spontaneous stacking of 2D nanosheets, resulting in thick COF laminates, blocking the access to surface-active catalytic sites and sabotaging mass transfer of electrolytes, reactants, and products. Second, their conjugated π-electron skeletons may open few-eV intrinsic bandgaps, impairing efficient electron transfer.

Received: December 8, 2020
Accepted: January 21, 2021
Published: January 25, 2021
Creating nanohybrids of 2D-COFs and carbon nanotubes (CNTs) may overcome the above challenges because CNTs can serve as spacers to prevent the stacking of 2D-COF and provide fast electron transfer paths.\textsuperscript{22–26} Along these lines, CNTs have been used to synthesize composites with 2D graphene or g-C\textsubscript{3}N\textsubscript{4} nanosheets.\textsuperscript{27–31} Further, intermolecular charge transfer may occur between CNTs and their surface adsorbates, which have been explored to modulate the adsorbates' catalytic activity.\textsuperscript{10,31–34} Composites can be formed by metallic, ionic, or covalent bonds. However, precise control of these strong chemical bonds is difficult, and the formation of these strong chemical bonds can also significantly interrupt the intrinsic properties of constituting components. Alternatively, 2D crystals have been assembled into van der Waals heterostructures (vdWHs) by stacking multiple 2D layers on top of each other, representing a different way to form crystals.\textsuperscript{35,36} In a recent study, 1D vdWHs were synthesized by growing boron nitride or molybdenum disulfide crystals on CNTs.\textsuperscript{37} We envision that coaxial 1D vdWHs can be formed by the peak at a chemical shift of 152 ppm. The peak at 1658 cm\textsuperscript{-1} can be assigned to imine (C=N) bonds in the framework. The \textsuperscript{13}C solid-state nuclear magnetic resonance (ssNMR) spectrum exhibits several peaks, which can be assigned to the predicted atomic structure of the TAPTt-COF (Figure S2). The formation of the imine bond can be further confirmed by the peak at a chemical shift of ~152 ppm. An AFM image and the corresponding height profiles of pristine TAPTt-COF (Figure S3) exhibits a large nanosheet (~2 × 4 μm\textsuperscript{2}) with a thickness of about 1.5 nm (4 atomic layers), confirming its 2D structure. Small-diameter multiwalled CNTs (MWCNTs) used in this study have smooth and clean surfaces (see TEM images in Figure S4). In comparison,
TEM images in Figure 1b–d show that seamless COF shells with varied thicknesses are formed on CNTs. The thickness of the COF shells can be precisely controlled at a nanometer-scale precision. Figure 1b–d display the thickness of COF shells is 4.2, 3.0, and 1.9 nm in the 1D vdWHs synthesized using COF precursors to CNTs at the mass ratio ranging from 4, 2, to 1 (Table 1).

### Table 1. Physiochemical Properties of TAPTt-COF, CNTs, and CC-X 1D vdWHs

| samples     | $m_{\text{COF}}$/ $m_{\text{precursor}}$ | thickness of COF shell (nm) | SSA (m² g⁻¹) | COF mass loading (%) |
|-------------|------------------------------------------|----------------------------|---------------|---------------------|
| CC-4        | 1                                        | 4.2 ± 0.5                  | 629           | 47.3                |
| CC-3        | 2                                        | 3.0 ± 0.4                  | 436           | 29.7                |
| CC-2        | 4                                        | 1.9 ± 0.2                  | 296           | 18.9                |
| TAPTt       |                                          |                            | 1059          |                     |
| MWNT        |                                          |                            | 112           |                     |

*The thickness was measured by TEM. *The mass loading was determined by DTG.

Strong $\pi-\pi$ interactions occur between CNTs and pyrene groups in TTAP, and we expect that such interactions play a critical role in guiding the formation of the 1D core–shell structured vdWHs. Without the presence of CNTs, pristine TAPTt-COF self-assemblies into microspheres with a diameter of about 2–3 μm, as shown in the scanning electron microscope (SEM) images in Figure S5. These COF microspheres contain well-aligned nanochannels around 2.5 nm wide, as confirmed by TEM observation shown in Figure S6, consistent with a molecular model of this type of COF. In contrast, only tubular structures are observed in the SEM images of CC-X vdWHs (Figure S7). Although the COF shells’ morphology changes significantly by the CNT cores, they retain their chemical characteristics. Figure S8 shows that their FTIR spectra are similar to that of pristine TAPTt-COF. Their XPS survey scans (Figure S9) and the corresponding high-resolution X-ray photoelectron spectroscopy (XPS) spectra of C1s, N1s, and S2p are virtually identical to that of pristine TAPTt-COF (Figure S10–S12). Figure S13 shows that O exists in chemisorbed water on CNTs and CC-X vdWHs with a low O content (<3 atom %). It should be noted that the XPS results indicate a low concentration of oxygenated functional groups, which were considered as active catalytic sites in a previous study.

Powder X-ray diffraction (XRD) patterns of pristine TAPTt-COF, CC-3, and CNTs are presented in Figure 1e. TAPTt-COF shows an XRD pattern consistent with its simulated eclipsed stacking model (orthorhombic, $a = 33.0 \, \text{Å}, b = 44.6 \, \text{Å}, c = 6.5 \, \text{Å}$, $\alpha = \beta = \gamma = 90^\circ$, Figure S14). The distinctive peaks at $2\theta = 3.38^\circ$, 5.35$^\circ$, and 6.67$^\circ$, which can be assigned to the (100), (200), and (220) planes, respectively. There is an interlayer d-spacing of ~0.38 nm from the most intense (001) reflection at a $2\theta$ of 23.35$^\circ$ (inset of Figure 1e, Cu Kα, $\lambda = 1.5406 \, \text{Å}$). In comparison, the CC-3 VdWH displays the features of TAPTt-COF and a broad peak from the (001) diffraction of CNTs at ~25$^\circ$. A different peak emerges at $2\theta = 7.59^\circ$, assigned to the (111) reflection of TAPTt-COF in a staggered stacking model (Figure S15). We assume the highly flexible imine bond in the TAPTt structure could allow the bending of the COF shell to the surface curvature of the carbon nanotube core. $^{41}$ $N_2$ physisorption isotherms and corresponding pore size distribution profiles are displayed in Figure 1f and Figure S16. TAPTt-COF exhibits a large specific surface area of 1059 m² g⁻¹ with abundant mesopores at ~2.5 nm. The specific surface area of CC-X vdWHs is listed in Table 1, showing a decreasing trend from 629 to 296 m² g⁻¹ with reducing COF shell thickness. Their pore size distribution profiles (Figure S16) show a different pore at ~1.6 nm, which can be assigned to such pores in TAPTt COF packed in the staggered stacking model (Figure S15).

The mass loading of TAPTt-COF in CC-X vdWHs was determined by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG). Figure 1g shows the representative TGA and DTG profiles of CC-3. The DTG profile’s deconvolution reveals two distinctive groups of peaks at 440 and 536 °C and >600 °C, which can be attributed to the thermal decomposition of TAPTt-COF and CNTs (Figure S17), respectively. The mass loading of COF in CC-3 is 29.7 wt % (Table 1), similar to the mass ratio between CNT and COF precursors (2:1). The mass loadings of COF in CC-4 and CC-2 exhibit the same agreement (inset of Figure 1g and Figure S17). Overall, different physicochemical characterization results confirm that our in situ wrapping method can precisely control COF shells’ thickness in the resulting 1D core–shell structured vdWHs.

### Electro catalytic Properties.

The electrocatalytic performances of CC-X vdWHs and several commercial catalysts as references were evaluated in O₂-saturated 0.1 M KOH electrolyte. Figure 2a shows their ORR linear sweep voltammetry (LSV) curves collected on rotary ring-disc electrode (RRDE). Their half-wave potentials ($E_{1/2}$) are listed in Table 2 for comparison. There is a clear trend that the electrocatalytic activity of CC-X vdWHs depends on their COF shells’ thickness. CC-3 exhibits the highest activity for ORR activity among the three vdWHs with the highest $E_{1/2}$ of 0.828 V (vs reversible hydrogen electrode (RHE)), which is also much higher than that of pristine TAPTt-COF at 0.741 V, CNTs at 0.698 V, and a physical mixture of TAPTt-COF and CNT at 0.761 V (at a mass ratio of 1:2, denoted as CC-P, see the Methods for details). The electron transfer number ($n$) and the selectivity to H₂O₂ selectivity are calculated and compared in Figure 2b. CC-X vdWHs follow a stable 4e⁻ ORR pathway in the tested potential window. The $n$ of CC-3 is ~3.86, close to that of 20 wt % Pt/C at 3.95 (Figure S18). Further, Koutecky−Levich (K−L) plots of different samples are compared to envisage their kinetic properties (Figure S19). The electron-transfer numbers were also determined from the K−L plots at 0.7 V_RHE, and the results are listed in Table 2.

The kinetic current densities ($j_k$) at 0.6 V_RHE of different samples are compared in Figure 2c. The $j_k$ of CC-3 (50.17 mA cm⁻²) and CC-2 (38.19 mA cm⁻²) are much higher than that of CC-1 (14.86 mA cm⁻²) and CC-P (9.37 mA cm⁻²). Besides, the $j_k$ of CC-3 is also higher than that of 20 wt % Pt/C (46.57 mA cm⁻²). Assuming TAPTt COF or Pt as the active catalytic component, the mass-normalized kinetic current density ($j_{k,\text{mass}}$) was calculated and listed in Table 2. Figure 2c shows that the $j_{k,\text{mass}}$ decreases with an increase in the COF shell thickness. CC-2 has the largest $j_{k,\text{mass}}$ of 1.01 A mg⁻¹, which is ~16% higher than that of CC-3 (0.84 A mg⁻¹) and over 30 times larger than that of TAPTt-COF (0.03 A mg⁻¹). However, because the mass loading of COF in CC-2 is lower than that in CC-3, CC-3 exhibits better overall catalytic performance for ORR. The stability test results shown in Figure 2d indicate that CC-3 has better stability than Pt/C. It retains 94% of its initial current density after the 24-h
chronoamperometric test at 0.4 \( V_{\text{RHE}} \). In comparison, Pt/C lost 24\% of its initial current density in 12 h. CC-S also exhibits good methanol tolerance (inset of Figure 2d).

The OER performance was also assessed in 0.1 M KOH electrolyte. Figure 2e displays the LSV curves of different samples. TAPTt-COF, CNTs, and CC-P show negligible OER catalytic activity. In contrast, CC-X vdWHs have much higher activities (Table 2). Among the three samples, CC-3 demonstrates the best catalytic performance with the lowest overpotential (\( \eta_{10} \)) of 389 mV to achieve the current density.

Table 2. Electrocatalytic Performances for ORR and OER of Different Catalysts

|         | \( E_{1/2} \) (V) | \( n^a \) | \( n^b \) | \( j^c_\text{max} \) (mA cm\(^{-2}\)) | \( \eta_{10} \) (mV) | Tafel slope (mV dec\(^{-1}\)) | TOF \( ^c \) (s\(^{-1}\)) | \( R_{\text{CT}} \) (ohm) |
|---------|------------------|---------|---------|-----------------|-----------------|-----------------|--------------------------|------------------|
| CC-4    | 0.771            | 3.62    | 3.64    | 14.86           | 0.16            | 457             | 122                      | 0.0242           |
| CC-3    | 0.828            | 3.86    | 3.89    | 50.17           | 0.84            | 389             | 101                      | 0.134            |
| CC-2    | 0.799            | 3.90    | 3.91    | 38.19           | 1.01            | 409             | 100                      | 0.138            |
| TAPTt   | 0.741            | 3.45    | 3.42    | 6.21            | 0.03            | 605             | 158                      | 0.00288          |
| MWCNT   | 0.698            | 3.21    | 3.14    | 3.60            | 0.03            | 751             | 228                      | 0.00288          |
| CC-P    | 0.761            | 3.54    | 3.57    | 8.37            | 0.13            | 578             | 153                      | 0.0114           |
| Pt/C    | 0.865            | 3.95    | 3.96    | 46.57           | 1.16            |                 |                          |                  |

\( ^a \) Determined from RRDE tests at 0.7 \( V_{\text{RHE}} \). \( ^b \) Calculated from K-L plots at 0.7 \( V_{\text{RHE}} \). \( ^c \) Calculated at \( \eta = 400 \) mV. \( ^d \) Obtained at \( \eta = 350 \) mV.

Figure 2. Electrocatalytic performance. (a) ORR RRDE-LSV curves and (b) calculated \( \eta \) and \( H_2O_2 \) %. (c) Comparison of \( \eta \) and \( j_K \) at 0.6 \( V_{\text{RHE}} \). (d) ORR stability and methanol tolerance test (inset) of CC-3. (e) OER-LSV curves and Tafel plots (inset). (f) Comparison of Tafel slopes and TOFs. (g) OER EIS Nyquist plots. (h) Faradaic efficiency and (i) OER stability of CC-3. (j) Comparison of recently reported bifunctional oxygen electrocatalysts with CC-3.
The inset of Figure 2f shows Tafel plots of different samples, and their Tafel slopes are compared in Figure 2f. CC-3 and CC-2 have comparable Tafel slopes of 101 and 100 mV dec⁻¹, respectively, indicating similar OER kinetics.

The current densities of different samples were further normalized according to their electrochemically active surface area (ECSA, measured by the cyclic voltammetry (CV) scanning method, Figure S20). The ECSA (Figure S21) suggests a similar performance trend as that in Figure 2d, except that the current density difference between CC-3 and CC-2 is reduced. Assuming that the active catalytic sites are on TAPTt-COF, we calculated the turnover frequency (TOF) of our different samples, as shown in Figure S22 (see the Methods for details). The TOFs at a η = 400 mV are compared in Figure 2f. The TOF of CC-2 at 0.138 s⁻¹ is slightly higher than that of CC-3 at 0.134 s⁻¹, suggesting its higher intrinsic activity, which is consistent with the results of their catalytic activity for ORR.

Electrochemical impedance spectroscopy (EIS) was used to determine the charge transfer resistance (Rct). A Nyquist plot is shown in Figure 2g, and the values of Rct determined at η = 350 mV are listed in Table 2. Rct depends on the thickness of the COF shells. Figure 2h shows that CC-3 delivers a near-unity Faradaic efficiency (99.2%), as determined by an RRDE method.42 It also displays excellent stability with less than 4% overpotential increment in the 24-h chronopotentiometric stability test under 10 mA cm⁻² (Figure 2i). The inset of Figure 2i shows a photo of oxygen bubbles on a CC-3 electrode.

We further compared ORR E₁/₂ and OER η₁₀ of CC-3 with recently reported metal-free and carbon-based bifunctional oxygen electrocatalysts (listed in Table S1). The potential difference (ΔE) between the E₁/₂ and η₁₀ collected in 0.1 M KOH electrolyte is calculated to compare their bifunctional catalytic activity. As displayed in Figure 2j, CC-3 shows the smallest ΔE of 791 mV. Alternatively, we also compiled a catalytic activity atlas by plotting ORR E₁/₂ against OER η₁₀. As shown in Figure S23, CC-3 is located at the bottom-left, suggesting one of the best catalytic performances among recently reported metal-free carbon electrocatalysts.12,29,32,43

Origin of Catalytic Activity. The electrocatalytic performance test results above suggest that the ORR and OER activity of 1D CC-X vdWHs depends strongly on the thickness of COF shells. We combined theoretical and spectroscopic studies to understand this dependence and explore the origin of their superior catalytic activity. We first analyzed electronic interactions by DFT calculations. The atomic geometry optimized CC-X vdWHs was modeled as thienothiophene moieties sitting on a graphene substrate. Figure 3a shows that the graphene substrate (electron-deficient, blue color) injects...
abundant delocalized electrons to thienothiophene moieties (electron-rich, yellow color), resulting in the n-doping effect to the COF shell. The delocalized electrons, which can be treated as excessive carriers, can change the COF shell electronic properties and, consequently, its electrochemical activity.56

We hypothesize that the COF shell’s excessive carriers should follow the well-established carrier continuity equation, which describes the decaying of excessive carriers in semiconductors as schematically illustrated in Figure S24.57 To prove our hypothesis, we compared the near-surface carrier density of CC-X vdWHs and pristine TAPTt-COF by applying the Mott−Schottky analysis.58 As shown in Figure S25, their Mott−Schottky plots (reciprocal square root of capacitance vs potential) all exhibit positive slopes, confirming the n-doping in the CC-X vdWHs.59 The value of this slope is inversely proportional to the near-surface carrier density. The smallest slope of CC-2 indicates its highest carrier density among the CC-X vdWHs (Table 3). We further plotted the reciprocal of the Mott−Schottky slopes as a function of the COF shell thickness in CC-X vdWHs in Figure S26. The fast decaying trajectory can be well fitted to the solution of carrier continuity equation at steady state.56 Thus, the COF thickness-dependent catalytic activity can be explained by the weakened electronic interaction between COF and CNT when the COF-shell thickness increases.

We further probed the n-doping effects in CC-X vdWHs by measuring their indirect bandgap using UV−vis DRS and near-surface work function (Φ) using UPS. Figure 3b shows that the bandgap of CC-X vdWHs decreases with the reduction of the COF shell thickness. TAPTt-COF has a bandgap of 2.08 eV, and CC-4, CC-3, and CC-2 have a bandgap of 1.58, 0.46, and 0.04 eV, respectively, approaching the bandgap of CNTs (0 eV, Table 3). Notably, the physically mixed CC-P has a bandgap of 1.99 eV, similar to that of TAPTt-COF, indicating that the bandgap modulation by CNTs is only possible when there are strong interactions between COF shells and CNTs. Further, the change of Φ measured by UPS confirms the same trend (Table 3). USP spectra in Figure 3c show that the valence band maximum (VBM) upshift closer to the Fermi level in CC-X vdWHs with thinner COF shells as a result of higher delocalized electron density.

Based on the above results, we propose that the superior catalytic activity of CC-X vdWHs is related to the n-type electronic interaction between CNTs and COF shells. The n-doping lowers COF shells’ bandgap and work function, leading to a reduced charge transfer barrier between COF shells and adsorbed oxygen intermediates.60 Further, CC-2, with the thinnest COF shell, experiences the most substantial n-doping, thus exhibiting the highest catalytic activity for ORR and OER. However, CC-3 contains a higher mass ratio of COF, which translates into a significantly increased active site number and better catalytic performance. Overall, CC-3 was identified as the optimal catalyst among the three CC-X vdWHs.

We further carried out theoretical calculations and spectroscopic studies to confirm the above-proposed origin of catalytic activity and elucidate the active catalytic center for oxygen redox reactions. Using the elementary steps and parameters proposed for ORR in previous studies,61,62 we calculated the free energy diagram of ORR intermediates adsorbed on possible active sites of TAPTt-COF. All atoms in the proposed model were allowed to relax. DFT results (Figure S27) show that the C−S region on the thienothiophene moiety is the only possible active site. The initial O₂ adsorption preferentially takes place at a C atom neighboring an S atom in the thienothiophene ring. After accepting a proton−electron pair, the OOH* intermediate diffuses to the S atom and proceeds along the dissociative ORR pathway. Figure S28 shows that all other atoms are either inert for the initial O₂ adsorption or have weak adsorbate binding properties, ruling out their possibility as active sites.

Next, we utilized operando FTIR to verify the proposed active catalytic center on CC-3 during ORR. Figure 3d shows the operando FTIR spectra collected under open circuit potential (V OC) and different ORR potentials. The IR bands associated with the structure of TAPTt-COF are mostly unchanged, confirming its excellent electrochemical stability. When different ORR potentials were applied, several different features emerge, which are associated with varying intermediates of reaction, as displayed in Figure 3e. The peaks at 860 and 865 cm⁻¹ can be assigned to the O−O stretching (μ₂−O) in O₂* or OOH* intermediates.63 The S−O stretching (μ₁−O) peak at 1056 cm⁻¹ is close to our DFT-calculated frequency of 1066 cm⁻¹. The O−H bending in S=O−H (δO−H) at 1162 and 1267 cm⁻¹ and the S=O stretching mode (μ₁−O) at 1335 and 1425 cm⁻¹ originate from intermediates formed along the dissociative ORR pathway. Further, the intensity of these S−O peaks increases under lower applied potentials, which is consistent with the reaction pathway determined from our DFT calculations.64 Thus, both theoretical calculations and spectroscopic studies confirm that the predesignated C−S region on the thienothiophene moiety of TAPTt-COF is the active catalytic center for oxygen redox reactions.

### Application in ZABs

We further demonstrated the application of CC-3 as an efficient bifunctional O₂ electro-catalyst to enable high-performance rechargeable ZABs. The details of battery assembly are described in the Methods. Figure S29 shows that the CC-3 ZAB has an open circuit potential of 1.477 V, which is comparable to 1.489 V of the ZAB assembled using commercial Pt/C and IrO₂/C catalysts (denoted as Pt−Ir/C). Figure 4a shows galvanodynamic charge/discharge profiles of two ZABs. The CC-3 ZAB delivers a maximum power density of 85 mW cm⁻², which is 21% higher than that of the Pt−Ir/C ZAB (74 mW cm⁻²). Under the discharging current density of 10 mA cm⁻², the capacity of the CC-3 ZAB is 714 mAh g⁻¹, comparable to 712 mAh g⁻¹ of the Pt−Ir/C ZAB (Figure 4b). Under the high discharging current density of 40 mA cm⁻², the CC-3 ZAB outperforms the Pt−Ir/C ZAB (696 vs. 684 mAh g⁻¹, see the inset of Figure 4b).

The ZAB cycling performance was evaluated by 120 discharging/charging cycles (j = 10 mA cm⁻², charge/discharge capacity is 5 mAh cm⁻² per cycle, Figure 4c). Both ZABs show similar performance at the first cycle with a
comparable round-trip efficiency of 60.0 and 61.5%, respectively (see the inset on the left in Figure 4c). After 30 cycles, the efficiency of the CC-3 ZAB declines slightly to 59.0%, while that of the Pt–Ir/C ZAB quickly drops to 55.3%. After 120 cycles, the CC-3 ZAB still retains a high efficiency of 55.1%. We also recorded ex situ XPS spectra of CC-3 after the 120-cycle rechargeability test. Figure S30 shows minor changes in N1s spectra, indicating the high electrochemical stability of imine bonds in TAPTt COF. In contrast, C1s, O1s, and S2p spectra exhibit substantial changes. Intensified C−O and O−O features are found in the deconvoluted C 1s spectrum. The O1s peak also shifts to the lower binding energy of 531.6 eV, which can be attributed to C−O and S−O chemical bonds’ formation. A different peak emerged in the S2p spectrum at 168.8 eV, which can be assigned to S−O chemical bonds, confirming the adsorption of O intermediates on S.65 These XPS results are consistent with our DFT calculations and operando FTIR results, further establishing the C=S region in thienothiophene as the active catalytic center for oxygen redox reactions. The poststability XRD and TEM measurement also confirmed the COF shells’ crystal structure could be well retained, suggesting that TAPTt COF has good electrochemical stability (Figure S31).

CONCLUSIONS

In summary, we report a metal-free and carbon-based coaxial 1D vdWH, which has a CNT core and TAPTt-COF shells with a tunable thickness from 2 to 4 nm. At the COF shell thickness of 3 nm, the optimal CC-3 vdWH can catalyze the OER via the 4e− pathway to deliver a TOF of 0.134 s−1 at an overpotential of 400 mV. The small potential difference between ORR E1/2 and OER η10 of 791 mV outperforms most recently reported metal-free bifunctional oxygen electrocatalysts. It enables high-performance rechargeable ZABs with a large specific capacity of 696 mAh gZn−1 (j = 40 mA cm−2) and excellent cycling stability. Using DFT calculations, UV–vis DRS, and UPS analysis, we show that the strong n-type electronic interaction between CNTs and COF shells is the origin of the significantly improved catalytic activity. Further, we provide a quantitative explanation of the COF shell thickness-dependent catalytic activity by the carrier decay model, providing mechanistic insights into the function of such heterostructured catalysts. The well-defined chemical structure further pinpoints the C=S region on the thienothiophene moiety of TAPTt COF as the active catalytic center through our theoretical calculations, experimental operando FTIR, and ex situ XPS studies. Our synthesis strategy demonstrated here affords an alternative approach to design and synthesize various multidimensional vdWHs for exploring fundamental physics and chemistry,
well as practical applications in electrochemistry, electronics, photonics, and beyond.

**METHODS**

**Material Preparation.** MWCNTs (FT9000, CNano, 10−25 nm in diameter) were first purified by a 2 h thermal treatment at 300 °C in air and then dispersed in 3 M HCl for 6 h to remove amorphous carbon and metal residues. Purified CNTs were washed with deionized water and then dried under vacuum. Afterward, CNTs were thermally annealed in Ar with deionized water and then dried in a vacuum oven. Subsequently, CNTs were dispersed in water/2-propanol (v/v:1/9) solution by bath sonication for 60 min. To reach a concentration of 5 mg mL⁻¹, CNTs were sonicated at a concentration of 5 mg mL⁻¹. TAPTt-COF and CNTs at a mass ratio of 1:2. The mixture was allowed to react for 2 days, followed by stirring for an additional 3 days. After cooling to room temperature, the solid products were recovered by centrifugation and repeatedly washed with pure DMAC before dried under vacuum.

**Characterization.** The FTIR spectra were collected on an FTIR spectrometer (Nicolet 6700, Thermo Scientific) in the attenuated total reflection mode. The operando tests were performed on the same FTIR spectrometer with an in situ electrochemical cell (PIKE Technologies). The ssNMR spectra were collected on an NMR spectrometer (Avance III, Bruker). N₂ physisorption isotherms were taken on a SEM (Ultra Plus, Zeiss) and a TEM (JEM-2200, JEOL) with a Cu Kα X-ray source. Electron microscope images were taken on a SEM (Ultra Plus, Zeiss) and a TEM (JEM-2200, JEOL) under an acceleration voltage of 80 kV. UV−vis DRS spectra were collected on an XPS spectrometer (K-Alpha+, Thermo Scientific). N₂ physisorption isotherms were recorded on a gas adsorption analyzer (iQ2, Quantachrome) at 77 K.

**Electrocatalyst Performance Tests.** Electrocatalysts' electrochemical performance was evaluated using an electrochemical workstation (760E, CHI) using the three-electrode configuration in 0.1 M KOH electrolyte. A Pt mesh, and a precalibrated Hg/HgO electrode (0.1 M NaOH) served as the counter and the reference electrodes, respectively. All potentials reported were corrected to the reversible hydrogen electrode (RHE).

For ORR tests, commercial Pt/C (20 wt %, Vulcan-XC-72R, Sigma) was tested under identical loading as the references. Selectivity toward H₂O₂ formation (H₂O₂%) and the ORR electron transfer number (n) were calculated from experimental data obtained using RRDEs in O₂ saturated electrolytes by eq 1 and (2), respectively.

\[
\text{H}_2\text{O}_2\% = 200 \times \frac{i_{\text{ring}} / N}{i_{\text{disk}} + i_{\text{ring}} / N} \tag{1}
\]

\[
n = 4 \times \frac{i_{\text{disk}}}{i_{\text{disk}} + i_{\text{ring}} / N} \tag{2}
\]

where \(i_{\text{ring}}\) and \(i_{\text{disk}}\) are the currents obtained from the Pt ring and GC disk, respectively. N is the calibrated collection efficiency. The electron transfer number (n) and \(i_{\text{k}}\) were also calculated using the K−L equation.

\[
1/i = 1/j_k + 1/j_k = 1/Bo^{1/2} + 1/j_k \tag{3}
\]

\[
B = 0.62nFC_0(D_o)^{1/2}/\omega^{1/6} \tag{4}
\]

\[
j_k = nFC_0 \tag{5}
\]

where \(j_{\text{p}}\) is the measured current density, \(j_k\) and \(j_l\) are the kinetic- and diffusion-limiting current densities, \(\omega\) is the angular velocity, \(n\) is the transferred electron number, \(F\) is the Faraday constant (96485 C mol⁻¹), \(C_0\) is the saturated concentration of O₂ in 0.1 M KOH at room temperature, \(D_0\) is the diffusion coefficient of oxygen, \(v\) is the kinematic viscosity of the electrolyte at room temperature, and \(k\) is the electron-transfer rate constant.

For OER tests, the Faradaic efficiency was assessed on an RRDE in Ar saturated 0.1 M KOH electrolytes. The Pt ring was biased at 0.4 V RHE, and the GC disk was biased at 1.5 V RHE. The H₂O₂ selectivity was calculated by eq 1 to determine the catalyst efficiency toward the 4-electron OER. The OER TOF of electrocatalysts was calculated by assuming all S−C regions in COF shells are active sites, using eq 6 shown below.

\[
\text{TOF} = \frac{i}{4 \times 96485 \times n} \tag{6}
\]

where \(i\) is the current and \(n\) is the number of active sites, which is calculated by eq 7.

\[
n = \frac{2 \times m \times w}{M_w} \tag{7}
\]

where \(m\) is the mass of electrocatalysts loaded on the electrode, \(w\) is the mass fraction of COF in electrocatalysts, and \(M_w\) is the molecular weight of a single unit of TAPTt-COF (~370 g mol⁻¹), containing two identical C−S regions. The electrodes for the water electrolyzer were prepared by coating 0.2 mg cm⁻² electrocatalysts on carbon clothes with a geometric dimension of 1 cm².

**Computational Method.** DFT calculations in this study were performed using the VASP code. Electron correlation was calculated using the generalized gradient approximation method with the functional developed by Perdew, Burke, and Ernzerhof. Core electrons were considered using the projector augmented wave method.

The valence electrons were described by expanding the Kohn−Sham wave functions in a plane-wave basis set, with a kinetic cutoff of 400 eV. Convergence was established when the forces of each atom were lower than 0.05 eV Å⁻¹. A γ-point sampling was used for all calculations. The reaction free energies of ORR were calculated using the computational hydrogen electrode method.

**Zn−Air Battery Tests.** Air electrodes were prepared by depositing electrocatalysts on carbon cloth gas-diffusion layers with a mass loading of 0.5 mg cm⁻². Reference air electrodes were prepared by depositing commercial Pt/C and IrO₂ catalysts (with a 1:1 molar ratio between Pt/Ir) at the same mass loading. A 6 M KOH solution with 0.2 M ZnCl₂ was used as the electrolyte. The total volume of electrolytes in every cell is about 20 mL. A piece of Zn foil (0.2 mm in thickness, 99.9%, Sigma) was used as the Zn electrode. The battery performance was evaluated in ambient air at ~25 °C using a battery tester (CT2001, Land).
ASSOCIATED CONTENT

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c10242.

FTIR, ssNMR, XPS spectra, AFM, SEM, and TEM images, XRD patterns, N2 physisorption isotherms, TGA profiles of TAPTt-COF, MWCNTs, and CC-X vdWHs; ORR LSV curves of Pt/C and CC-X vdWHs; CV curves and calculated C_{st} of CC-X vdWHs; ECSA-normalized OER LSV curves and TOFs of TAPTt-COF, CC-x, and CC-P; activity atlas of various bifunctional carbon electrocatalyst for ORR and OER; performance comparison of recently reported metal-free and carbon-based ORR and OER electrocatalysts; schematic illustration of carrier injection from CNTs to a COF shell; Mott–Schottky plots of TAPTt-COF and CC-X VdWHs; relationship between the reciprocal of the slope in the Mott–Schottky plot as a function of the COF shell thickness; free energy diagram of oxygen reaction intermediates on the most feasible S–C active site; DFT models of ORR intermediates adsorbed on other possible sites on TAPTt COF; open circuit potential vs time of ZABs assembled using CC-3 and Pt–Ir/C catalysts; XPS spectra, XRD patterns, and a TEM image of CC-3 after the ZAB cycling test (PDF)

AUTHOR INFORMATION

**Corresponding Authors**
Graeme Henkelman – Department of Chemistry and the Oden Institute for Computational and Engineering Sciences, The University of Texas at Austin, Austin, Texas 78712, United States; orcid.org/0000-0002-0336-7153; Email: henkelman@utexas.edu
Li Wei – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia; orcid.org/0000-0001-8771-2921; Email: lwei@sydney.edu.au
Yuan Chen – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia; orcid.org/0000-0001-9059-3839; Email: yuan.chen@sydney.edu.au

**Authors**
Chang Liu – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia
Fei Liu – State Key Laboratory of Applied Microbiology Southern China, Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, Guangdong Institute of Microbiology, Guangzhou S10070, Guangdong, China
Hao Li – Department of Chemistry and the Oden Institute for Computational and Engineering Sciences, The University of Texas at Austin, Austin, Texas 78712, United States; orcid.org/0000-0002-7577-1366
Junsheng Chen – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia
Jingyuan Fei – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia

**References**
(1) Zhao, X.; Pachfule, P.; Li, S.; Langenhahn, T.; Ye, M.; Schlesiger, C.; Praet, S.; Schmidt, J.; Thomas, A. Macro/Microporous Covalent Organic Frameworks for Efficient Electrocatalysis. J. Am. Chem. Soc. 2019, 141 (16), 6623–6630.
(2) Guo, J.; Lin, C. Y.; Xia, Z.; Xiang, Z. A Pyrolysis-Free Covalent Organic Polymer for Oxygen Reduction. Angew. Chem., Int. Ed. 2018, 57 (36), 12567–12572.
(3) Yang, S.; Yu, Y.; Dou, M.; Zhang, Z.; Dai, L.; Wang, F. Two-Dimensional Conjugated Aromatic Networks as High-Site-Density and Single-Atom Electrocatalysts for the Oxygen Reduction Reaction. Angew. Chem., Int. Ed. 2019, 58 (41), 14724–14730.
(4) Peng, P.; Shi, L.; Huo, F.; Mi, C.; Wu, X.; Zhang, S.; Xiang, Z. A Pyrolysis-Free Path toward Superiorly Catalytic Nitrogen-Coordi- nated Single Atom. Sci. Adv. 2019, 5 (8). No. eaaw2322.
(5) Li, B. Q.; Zhang, S. Y.; Wang, B.; Xia, Z. J.; Tang, C.; Zhang, Q. A Porphyrin Covalent Organic Framework Cathode for Flexible Zn–Air Batteries. Energy Environ. Sci. 2018, 11 (7), 1723–1729.
(6) Peng, P.; Zhou, Z.; Guo, J.; Xiang, Z. Well-Defined 2D Covalent Organic Polymers for Energy Electrocatalysis. ACS Energy Lett. 2017, 2 (6), 1308–1314.
(7) Feng, X.; Ding, X.; Jiang, D. Covalent Organic Frameworks. Chem. Soc. Rev. 2012, 41 (18), 6010–6021.
(8) Ding, S. Y.; Wang, W. Covalent Organic Frameworks (COFs): From Design to Applications. Chem. Soc. Rev. 2013, 42 (2), 548–68.

**Author Contributions**
4L.C.L., F.L., and H.L. contributed equally.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
We thank funding support from the Australian Research Council under the Future Fellowships scheme (FT160100107) and Discovery Programme (DP180102210), support from GDAS’ Special Project of Science and Technology Development (2019GDASYL-0104005 and 2020GDASYL-20200402001). H.L. and G.H. acknowledge the Welch Foundation (F-1841) and the Texas Advanced Computing Center for computational resources.

**REFERENCES**

Zixun Yu – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia
Ziwen Yuan – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia; orcid.org/0000-0002-3331-0668
Chaojun Wang – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia
Huiling Zheng – Department of Chemistry and the Oden Institute for Computational and Engineering Sciences, The University of Texas at Austin, Austin, Texas 78712, United States; orcid.org/0000-0001-8347-3724
Zongwen Liu – School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington 2006, NSW, Australia
Meiyong Xu – State Key Laboratory of Applied Microbiology Southern China, Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, Guangdong Institute of Microbiology, Guangzhou S10070, Guangdong, China; orcid.org/0000-0001-7726-4219
Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsnano.0c10242
Composite Electrocatalyst. 

ACS Nano

www.acsnano.org

2018

Mater.

ACS

Boronic Ester Based Covalent Organic Frameworks/Carbon Nano-

Nano 2018, 14 (44), No. 1801929.

ACS Nano

2018

2017, 1 (12), 1700209.

Adv. Mater. 2017, 29 (7), 1604685.

Adv. Mater. 2018, 8 (5), 1701620.

ACS Energy Lett. 2018, 3, 1690−1704.

ACS Catal. 2020, 10 (10), 5623−5630.

Adv. Mater. 2018, 30 (16), 5743−5749.

Adv. Mater. 2017, 29 (9), 6210−6217.

ACS Nano 2019, 13 (3), 3600−3607.

ACS Nano 2020, 8 (15), 5946−5953.

ACS Appl. Nano Mater. 2020, 3 (2), 1412−1419.

ACS Appl. Nano Mater. 2018, 1 (2), 1709−1712.

ACS Nano 2017, 14 (9), 3139−3145.

ACS Nano 2018, 13 (6), 3783−3788.

ACS Nano 2019, 14 (18), 2925−2930.

ACS Nano 2018, 8 (3), 1926−1931.

ACS Catal. 2020, 11 (13), 5182−5.

ACS Catal. 2017, 9 (14), 16042.

ACS Catal. 2016, 6 (5), 1501966.

ACS Catal. 2015, 7 (8), 2901−2910.

ACS Catal. 2014, 5 (17), 2930−2940.

ACS Catal. 2019, 11 (29), 16965−1666.

Adv. Mater. 2016, 28 (18), 9001−9006.

Adv. Mater. 2015, 27 (8), 1365−1372.

Adv. Mater. 2018, 30 (5), 1372−1385.

Adv. Mater. 2017, 29 (12), 128501.

Bio Energy Combust. Sci. 2018, 66, 141−175.

Chem. Rec. 2017, 17 (9), 1365−1372.

Chem. Rev. 2018, 118 (8), 3619−3676.

Chem. Sci. 2017, 8 (5), 3630−3636.

Chem. Soc. 2015, 137 (8), 2901−7.

Chem. Soc. 2016, 133 (6), 638−639.

Chem. Soc. 2002, 31 (6), 638−639.

Chem. Commun. 2017, 53 (47), 6303−6306.

Chem. Mater. 2019, 31 (6), 3218−3227.

Chem. Mater. 2018, 30 (15), 5367−5374.

Chem. Mater. 2017, 29 (3), 1501−1506.

Chem. Mater. 2016, 28 (11), 3319−3331.

Chem. Mater. 2015, 27 (8), 2901−2910.

Chem. Mater. 2018, 30 (7), 1696−1709.

Chem. Sci. 2011, 334 (6061), 1383−1385.

Chem. Sci. 2011, 334 (6061), 1383−1385.

Chem. Sci. 2011, 334 (6061), 1383−1385.
Batteries.

Highly-Efficient Metal-Free Bifunctional Electrocatalyst for Zn-Air
Enabling Hierarchically Porous Honeycombed Defective Carbon as
Y.; Wang, J. Robust Template-Activator Cooperated Pyrolysis
J. Am. Chem. Soc.

Commun.

Nørskov, J. K. Solvation Effects for Oxygen Evolution Reaction
2013

Electrolyte from the Mott-Schottky Plot.
Band Potential of a Semiconductor in Contact with a Metal or an
Wiley & Sons: Hoboken, NJ, 2007; pp 5

Delocalization Model from First Principles Calculations.

Rechargeable Zn-Air Batteries.
Electrocatalyst Derived from Metal-Organic Frameworks for
Lee, J. Y.; Zhao, D. A Metal-Free ORR/OER Bifunctional
Carbon
Doped Porous Carbon@Graphene Sandwich-Like Structured Com-
G.; Zhao, H.; Cai, W. Metal-Organic Framework Derived Nitrogen-
Ed.
2015

Paper: Flexible and Reversible Oxygen Electrodes. Angew. Chem., Int.
Ed. 2015, 54 (15), 1–6.

Liu, S.; Zhang, H.; Zhao, Q.; Zhang, X.; Liu, R.; Ge, X.; Wang,
G.; Zhao, H.; Cai, W. Metal-Organic Framework Derived Nitrogen-
Doped Porous Carbon@Graphene Sandwich-Like Structured Com-
posites as Bifunctional Electrocatalysts for Oxygen Reduction and
Evolution Reactions. Carbon 2016, 106, 74–83.

Qian, Y.; Hu, Z.; Ge, X.; Yang, S.; Peng, Y.; Kang, Z.; Liu, Z.;
Lee, J. Y.; Zhao, D. A Metal-Free ORR/OER Bifunctional Electrocatalyst Derived from Metal-Organic Frameworks for
Rechargeable Zn-Air Batteries. Carbon 2017, 111, 641–650.

Qu, K.; Zheng, Y.; Dai, S.; Qiao, S. Z. Graphene Oxide-
Polydopamine Derived N, S-Codoped Carbon Nanosheets as Superior Bifunctional Electrocatalysts for Oxygen Reduction and Evolution. Nano Energy 2016, 19, 373–381.

Jia, N.; Weng, Q.; Shi, Y.; Shi, X.; Chen, X.; Chen, P.; An, Z.;
Chen, Y. N-Doped Carbon Nanocages: Bifunctional Electrocatalysts for the Oxygen Reduction and Evolution Reactions. Nano Res. 2018, 11 (4), 1905–1916.

Zhang, J.; Zhao, Z.; Xia, Z.; Dai, L. A Metal-Free Bifunctional Electrocatalyst for Oxygen Reduction and Oxygen Evolution Reactions. Nat. Nanotechnol. 2015, 10, 444.

Yang, H. B.; Miao, J.; Hung, S.-F.; Chen, J.; Tao, H. B.; Wang,
X.; Zhang, L.; Chen, R.; Gao, J.; Chen, H. M.; Dai, L.; Liu, B.
Identification of Catalytic Sites for Oxygen Reduction and Oxygen Evolution in N-Doped Graphene Materials: Development of Highly Efficient Metal-Free Bifunctional Electrocatalyst. Sci. Adv. 2016, 2 (4), e1501122.

Lin, X.; Peng, P.; Guo, J.; Xiang, Z. Reaction Milling for Scalable Synthesis of N, P-Codoped Covalent Organic Polymers for Metal-Free Bifunctional Electrocatalysts. Chem. Eng. J. 2019, 358, 427–434.

Guo, Y.; Yao, S.; Gao, L.; Chen, A.; Jiao, M.; Cui, H.; Zhou, Z.
Boosting Bifunctional Electrocatalytic Activity in S and N Co-Doped Carbon Nanosheets for High-Efficiency Zn-Air Batteries. J. Mater. Chem. A 2020, 8 (8), 4386–4395.

Wang, H.-F.; Tang, C.; Zhang, Q. Template Growth of Nitrogen-Doped Mesoporous Graphene on Metal Oxides and Its Use as a Metal-Free Bifunctional Electrocatalyst for Oxygen Reduction and Evolution Reactions. Catal. Today 2018, 301, 25–31.

Xiao, X.; Li, X.; Wang, Z.; Yan, G.; Guo, H.; Hu, Q.; Li, L.; Liu,
Y.; Wang, J. Robust Template-Activator Cooperated Pyrolysis Enabling Hierarchically Porous Honeycombed Defective Carbon as Highly-Efficient Metal-Free Bifunctional Electrocatalyst for Zn-Air Batteries. Appl. Catal., B 2020, 265, 118603.

Wang, Z.; Yang, B.; Wang, Y.; Zhao, Y.; Cao, X. M.; Hu, P.
Identifying the Trend of Reactivity for sp² Materials: An Electron Delocalization Model from First Principles Calculations. Phys. Chem. Chem. Phys. 2013, 15 (24), 9498–9502.

Sze, S. M.; Ng, K. K., Physics and Properties of Semiconduc-
tors—A Review. Physics of Semiconductor Devices, 3rd ed.; John Wiley & Sons: Hoboken, NJ, 2007; pp 5–75.

Cardon, F.; Gomes, W. P. On the Determination of the Flat-
Band Potential of a Semiconductor in Contact with a Metal or an
Electrolyte from the Mott-Schottky Plot. J. Phys. D: Appl. Phys. 1978, 11 (4), L63–L67.

Herrmann, J.; Alfe, D.; Tkatchenko, A. Nanoscale π-π Stacked
Molecules Are Bound by Collective Charge Fluctuations. Nat.
Commun. 2017, 8 (1), 14052.

Cheon, J. Y.; Kim, J. H.; Kim, J. H.; Goddetti, K. C.; Park, J. Y.;
Joo, S. H. Intrinsic Relationship between Enhanced Oxygen Reduction Reaction Activity and Nanoscale Work Function of Doped Carbons. J. Am. Chem. Soc. 2014, 136 (25), 8875–8878.

Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.;
Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. J. Phys. Chem. B 2004, 108 (46), 17886–17892.

Gauthier, J. A.; Dickens, C. F.; Chen, L. D.; Doyle, A. D.;
Nørskov, J. K. Solvation Effects for Oxygen Evolution Reaction
Catalysis on IrO₂ (110). J. Phys. Chem. C 2017, 121 (21), 11455–
11463.

Vacque, V.; Sombret, B.; Huvenne, J. P.; Legrand, P.; Suc, S.
Characterisation of the O-O Peroxide Bond by Vibrational Spectrosc.
Spectrochim. Acta, Part A 1997, 53 (1), 55–66.

Noguchi, T.; Nojiri, M.; Takei, K.-i.; Odaka, M.; Kamiya, N.
Protonation Structures of Cys-Sulfinic and Cys-Sulfenic Acids in the Photosensitive Nitrile Hydratase Revealed by Fourier Transform Infrared Spectroscopy. Biochemistry 2003, 42 (40), 11642–11650.

Beamson, G.; Briggs, D. High Resolution XPS of Organic Polymers: The Sciecta ESCA300 Database, 1st ed.; Wiley, 1992.

Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved Adsorption Energies within Density-Functional Theory Using Revised Perdew-Burke-Ernzerhof Functionals. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59 (11), 7413–7421.

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

Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 1965, 140 (4A), A1133–A1138.