

# 1 A Thiadiazole-Based Covalent Organic Framework: A Metal-Free 2 Electrocatalyst toward Oxygen Evolution Reaction

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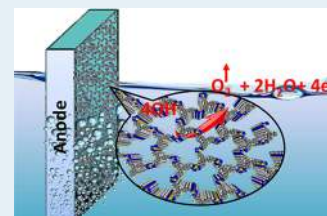
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Supporting Information

5 **ABSTRACT:** Covalent organic frameworks (COFs) have attracted surging interest lately due to  
6 their wide potential in several frontline application areas like gas storage, sensing, photovoltaics,  
7 fuel cells, active catalyst supports, and so on. However, only very few reports are available for the  
8 metal-free electrocatalysis over COFs. Herein, we developed a new thiadiazole-based COF, C4-  
9 SHz COF, through the reaction between 1,3,5-tris(4-formylphenyl)benzene and 2,5-dihydrazinyl-  
10 1,3,4-thiadiazole that possesses a very high specific surface area of 1224 m<sup>2</sup> g<sup>-1</sup>, unique molecular  
11 architecture, high porosity, and abundant active sites. The as-synthesized C4-SHz COF displayed  
12 superior electrocatalytic oxygen evolution reaction (OER) activity and excellent long-term  
13 durability. The electrocatalytic performance of the C4-SHz COF achieved a current density of 10 mA/cm<sup>2</sup> at an overpotential of 320  
14 mV. The higher activity of the C4-SHz COF could be attributed to the high Brunauer–Emmett–Teller surface area, porosity, and  
15 network structure of the  $\pi$ -conjugated organic building blocks, which allowed fast charge and mass transport processes. This work  
16 validates the promising potential of a metal-free COF electrocatalyst toward the OER and its capability to replace carbon-based  
17 electrocatalysts.

18 **KEYWORDS:** covalent organic frameworks (COFs), thiadiazole moiety, metal-free electrocatalyst, oxygen evolution reaction (OER),  
19 water splitting



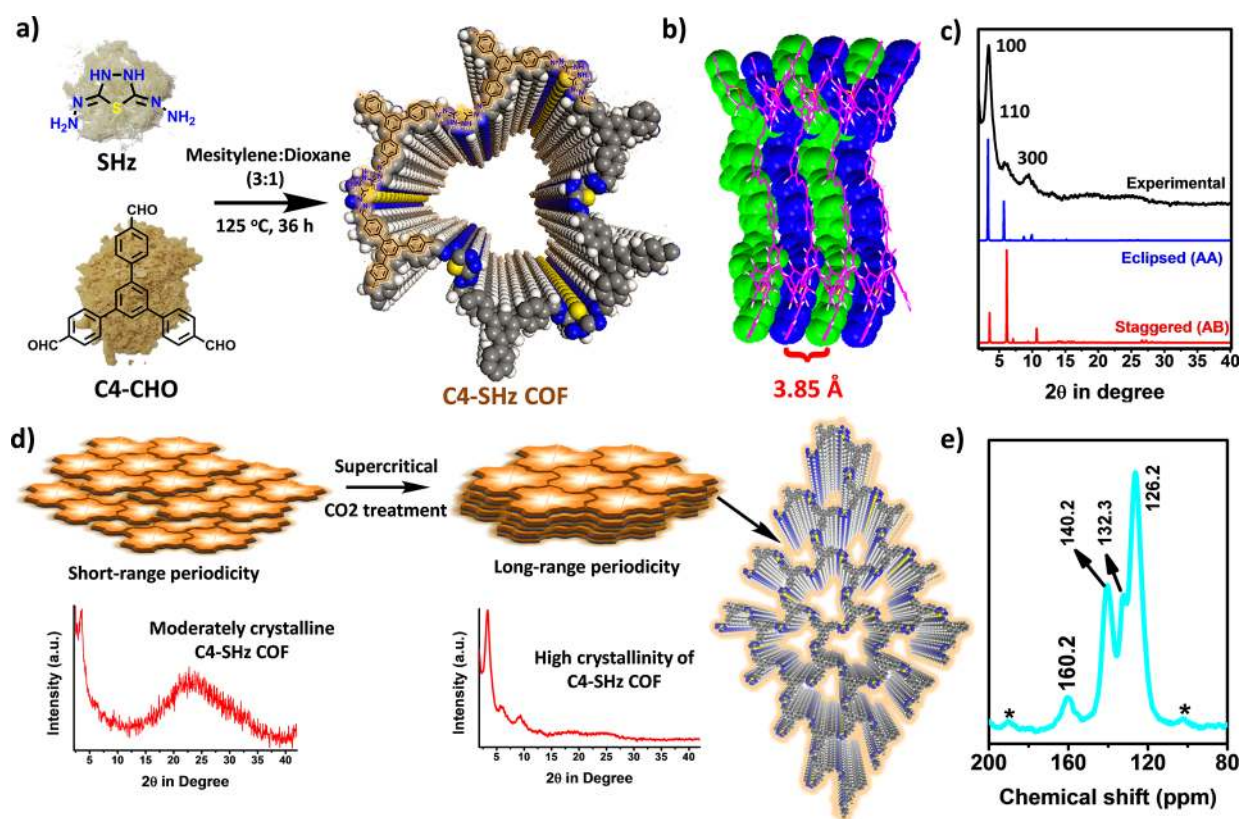
## 20 ■ INTRODUCTION

21 Rapid decay of fossil fuels combined with environmental crises  
22 associated with carbon emissions significantly affected the  
23 economy and ecology of the whole world. Thus, the demand  
24 for renewable energy is surging over the years, and electro-  
25 chemical water splitting can be considered as a green and  
26 promising technology<sup>1</sup> to overcome this problem. The  
27 electrochemical water splitting plays a crucial role in advanced  
28 energy technologies, such as solar fuel production, super-  
29 capacitor, metal–air batteries, etc.<sup>2–5</sup> Still, water oxidation  
30 (oxygen evolution reaction, OER) requires a higher energy  
31 input due to the involvement of the multi-electron transfer  
32 reaction pathway and its low efficiency. Hence, the  
33 commercialization of water splitting technology requires stable,  
34 highly active, and low-cost water oxidation electrocatalysts.  
35 Currently, precious transition metal oxide-based electro-  
36 catalysts such as RuO<sub>2</sub> and IrO<sub>2</sub> are highly active toward the  
37 OER from alkaline water. However, high cost, scarcity, and low  
38 stability hamper the utilization of clean and sustainable energy  
39 technologies<sup>6,7</sup> in this context. Thus, for the past couple of  
40 years, extensive efforts have been devoted for the development  
41 of earth-abundant, low-cost, and efficient transition metal-  
42 based electrocatalysts such as oxides, chalcogenides, phos-  
43 phides, nitride, metal-free catalysts, etc., for the OER.<sup>8–14</sup>  
44 However, most of the transition metal-based catalysts still  
45 suffer from lower catalytic activity, inferior conductivity, and  
46 poor operational durability.

Simultaneously, over the past few years, intensive research  
47 has been carried out for developing efficient metal-free  
48 catalysts.<sup>2,3</sup> Metal-free electrocatalysts have several unique  
49 advantages, such as their environment-friendly nature, earth-  
50 abundant, cost-effective, and resistance to a wide pH range.  
51 For electrochemical OER applications, several metal-free  
52 catalysts have been developed in recent times.<sup>15–17</sup> Among  
53 different metal-free porous nanomaterials, covalent organic  
54 frameworks (COFs)<sup>18,19</sup> are the emerging class of porous  
55 organic polymers with precisely controllable structural motifs  
56 linked through covalent bonds. COFs possess extraordinary  
57 properties like large surface area, high crystallinity, tunable  
58 pore size, and unique molecular architecture.<sup>20–24</sup> Due to these  
59 unique properties, COFs have been used in a wide range of  
60 applications.<sup>25–27</sup> High surface area, tunable structures with  
61 appropriate building blocks, and porous nature of the COFs  
62 made them ideal for electrocatalysis.<sup>28</sup> Accordingly, substantial  
63 progress has been made for the design and synthesis of COFs  
64 from low-cost monomer precursors. Till now, COFs have been  
65 explored as a support material of graphene, conductive carbon, 66

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**Figure 1.** Schematic presentation of the COF (a) proposed structure and (b) packing diagram. (c) Comparison of experimental PXRD pattern of the crystalline C4-SHz COF with simulated PXRD patterns of the C4-SHz COF. (d) Graphical representation of switching shortly to long-range periodicity. (e) Solid-state <sup>13</sup>C MAS NMR spectrum of the COF; the spinning sidebands are represented by asterisks.

67 carbon nanotubes (CNTs), etc., for electrocatalytic applica-  
 68 tions. For example, Kamiya et al. have reported covalent  
 69 triazine frameworks as support materials for Pt nanoparticle  
 70 and studied its ORR activity.<sup>29</sup> Mullangi et al. used flexible  
 71 COFs as support materials for electrocatalytic OER  
 72 applications.<sup>28</sup> Similarly, Aiyappa et al. designed Co-COF  
 73 and studied its OER activity,<sup>30</sup> whereas Fe and Co NPs  
 74 supported over COFs have been employed in electrochemical  
 75 oxygen reduction reaction (ORR).<sup>31</sup> Although there are very  
 76 few reports on the usage of COFs as photocathodes for light-  
 77 induced hydrogen evolution reaction (HER) via water  
 78 splitting,<sup>32</sup> the use of a crystalline COF as a metal-free OER  
 79 electrocatalyst has been rarely explored till date.<sup>33</sup>

80 In this article, we have introduced an unprecedented imine-  
 81 linked thiadiazole-based crystalline COF (C4-SHz COF) and  
 82 explored its catalytic activity in the electrochemical water  
 83 oxidation reaction. Through the general solvothermal protocol  
 84 (Schiff base condensation using acetic acid),<sup>26,27,30</sup> a nitrogen-  
 85 rich thiadiazole moiety has been incorporated in the polymeric  
 86 backbone of the C4-SHz COF, which exhibited superior  
 87 activity toward OER. The relevant characterization data  
 88 suggested that the C4-SHz COF possesses a high specific  
 89 surface area and crystalline metal-free organic framework  
 90 structure. The newly developed COF displayed an excellent  
 91 electrocatalytic activity and durability under alkaline pH  
 92 conditions, which is comparable to the other metal-free  
 93 electrocatalysts reported so far.

## RESULTS AND DISCUSSION

94

The thiadiazole-based imine-linked COF (C4-SHz COF) was  
 95 synthesized through the general Schiff base condensation  
 96 polymerization between 1,3,5-tris(4-formylphenyl)benzene  
 97 (C4-CHO) and 2,5-dihydrazinyl-1,3,4-thiadiazole (SHz)  
 98 under the solvothermal condition for 36 h (Figure 1a and  
 99 Figures S1–S3, Supporting Information). The resultant as-  
 100 synthesized imine-linked framework has shown a low sign of  
 101 crystallinity (Figure 1d), and this could often occur due to the  
 102 self-assembly through weak  $\pi$ - $\pi$  stacking interaction of  
 103 individual COF layers. To get the well-defined molecular  
 104 stacked framework, the as-synthesized C4-SHz COF material  
 105 was activated using supercritical carbon dioxide treatment  
 106 following the reported protocol by Medina et al.<sup>34</sup> The more  
 107 prominent desired peaks in X-ray diffraction for the post-  
 108 activated material is observed (Figure 1d), suggesting the well-  
 109 defined structure of pores. Surprisingly, the measured  $S_{\text{BET}}$   
 110 values are also mirroring this trend by narrowing the pore size  
 111 (Figure S4, Supporting Information).  
 112

The crystalline structure of the C4-SHz COF is resolved  
 113 through the experimental powder X-ray diffraction measure-  
 114 ment in combination with theoretical simulations and Pawley  
 115 refinement (Figure S5 and Tables S1 and S2, Supporting  
 116 Information). As seen in Figure 1c, a distinct peak at  $2\theta = 3.3^\circ$   
 117 is assigned to the 100 crystal plane of the COF. Additionally,  
 118 relatively weak peaks at  $2\theta = 5.8$  and  $9.9^\circ$  correspond to the  
 119 reflection from 110, and 300 planes are also observed. The  
 120 weak broad peak centered at  $2\theta = 20$ – $26^\circ$  (002 plane) is  
 121 possibly due to the interlayer  $\pi$ - $\pi$  stacking of the COF, and  
 122 distances between the individual 002 planes are ca. 3.85 Å  
 123

124 (Figure 1b). A probable 2D model structure was constructed  
 125 using Materials Studio 7 in the *P1* space group. An asymmetric  
 126 unit in the crystal structure and graphical representation of the  
 127 2D layered COF is shown in Figure S6 (Supporting  
 128 Information). The simulated PXRD pattern of the eclipsed  
 129 AA stacking model is well fitted with the experimental  
 130 diffraction data (Figure 1c). In contrast, the PXRD pattern  
 131 obtained from the AB stacking model deviates from the  
 132 experimentally observed data, especially in terms of peak  
 133 intensity ratios. The perfect agreement in favor of the  
 134 experimental X-ray pattern was further confirmed by Pawley  
 135 refinement [ $R_{\text{wp}} = 7.23\%$ ,  $R_p = 5.32\%$ ] (Figure S5). The unit  
 136 cell parameters were as follows:  $a = 31.00 \text{ \AA}$ ,  $b = 31.46 \text{ \AA}$ ,  $c =$   
 137  $7.70 \text{ \AA}$ ;  $\alpha = 99.26^\circ$ ,  $\beta = 87.67^\circ$ , and  $\gamma = 120.51^\circ$ .

138 The specific surface area and porous nature of the C4-SHz  
 139 COF were examined by conducting  $\text{N}_2$  adsorption–desorption  
 140 analysis at 77 K. As shown in Figure 2a, the C4-SHz COF

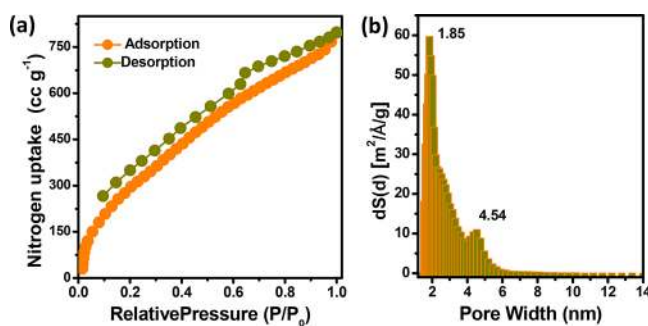


Figure 2. (a)  $\text{N}_2$  adsorption–desorption analysis of the C4-SHz COF and (b) NLDFT pore size distribution plots.

141 exhibits a combination of type I and IV isotherms. A significant  
 142 nitrogen uptake at low relative pressures ( $P/P_0 < 0.03$ )  
 143 followed by a gradual increase in adsorption at a higher  $P/P_0$   
 144 value suggested the distinctive features for the coexistence of  
 145 micropores and mesopores along with interparticle pores.<sup>35–38</sup>  
 146 The corresponding pore size distribution plot (Figure 2b), as  
 147 determined from the adsorption branch of the isotherm based  
 148 on nonlocal density functional theory (NLDFT), revealed the  
 149 presence of micropores and mesopores in our C4-SHz COF  
 150 material. The calculated BET (Brunauer–Emmett–Teller,  
 151  $S_{\text{BET}}$ ) surface area from this isotherm was  $1224 \text{ m}^2 \text{ g}^{-1}$ , and  
 152 the total pore volume was  $1.12 \text{ cc g}^{-1}$ . The simulated BET  
 153 surface area of the AA stacked model of the C4-SHz COF has  
 154 been computed using the DFTB calculations. The correspond-  
 155 ing simulated specific surface area was found to be  $2339 \text{ m}^2 \text{ g}^{-1}$   
 156 (Figure S7, Supporting Information). The noticeable distin-  
 157 ction in BET surface area from the experimental data is  
 158 related to the crystallinity of the COF material, and such  
 159 deviations were also reported for other imine-based  
 160 COFs.<sup>39–42</sup>

161 The structural growth and imine linkage formation of the  
 162 COF are confirmed by FTIR and  $^{13}\text{C}$  MAS NMR analyses. In  
 163 the FTIR spectrum of the C4-SHz COF (Figure 3a), the  
 164 absorption band at  $1693 \text{ cm}^{-1}$  corresponded to  $\text{C}=\text{N}$   
 165 absorption, which is also confirmed by the resonance signal  
 166 at  $160.2 \text{ ppm}$  in  $^{13}\text{C}$  NMR. The peak at  $3416 \text{ cm}^{-1}$  could be  
 167 attributed to  $\text{N}-\text{H}$  stretching vibration. The complete  
 168 utilization of the aldehyde sources was confirmed by the  
 169 missing peak at  $1698 \text{ cm}^{-1}$  in the IR spectrum and the absence  
 170 of aldehydic resonance peak at  $190 \text{ ppm}$  in  $^{13}\text{C}$  NMR. In the

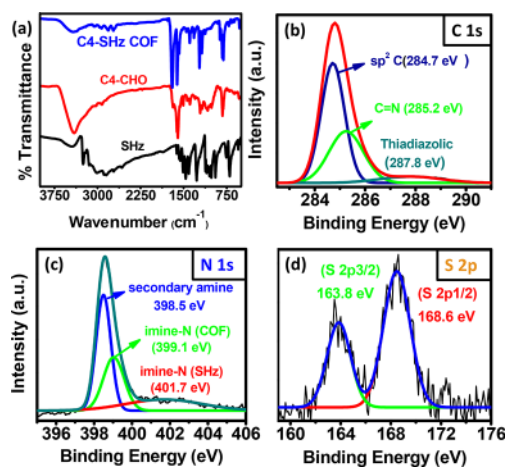
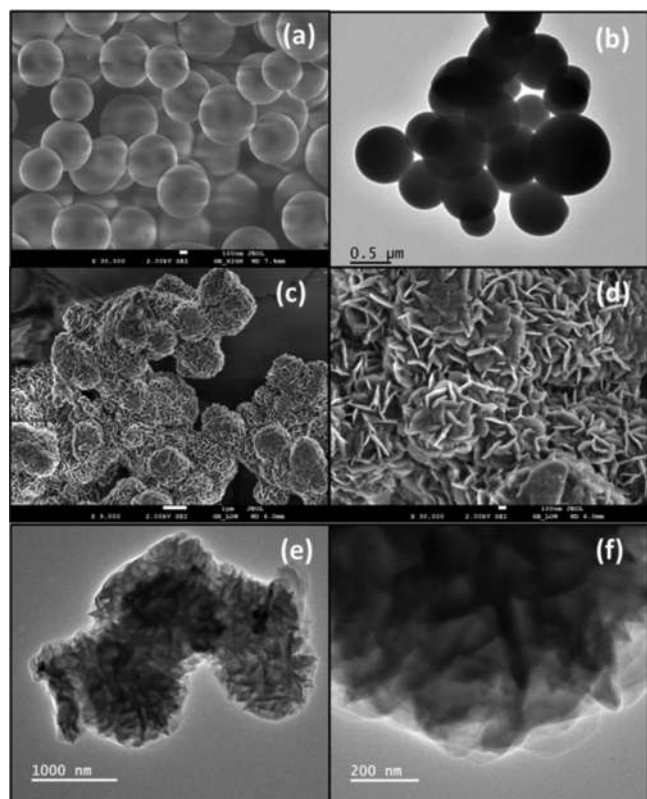


Figure 3. (a) IR spectrum of the C4-SHz COF along with the spectra of SHz and C4-CHO. (b) C 1s X-ray photoelectron spectroscopy (XPS). Deconvoluted high-resolution (c) N 1s XPS spectra and (d) S 2p XPS spectra of the thiadiazole-based COF.

spectrum in Figure 1e, the resonance signal at  $160.2 \text{ ppm}$  is  
 171 ascribed to the carbon atom adjacent to the S atom of the SHz  
 172 moiety. The peak at  $140.2 \text{ ppm}$  is indicative of substituted  
 173 quaternary carbons of the polymeric network. The resonance  
 174 peak at  $132.3 \text{ ppm}$  is attributed to the carbon atom of the  
 175 aldehyde moiety that connected to the imine carbon of the  
 176 organic framework. The additional peak at  $126.2 \text{ ppm}$   
 177 appeared due to the  $\text{sp}^2$ -hybridized aromatic carbons.  
 178

To gain further information about the surface chemistry and  
 179 chemical composition, we have carried out the XPS analysis of  
 180 the C4-SHz COF. As shown in Figure 3c, the N 1s spectrum  
 181 can be deconvoluted into three component peaks ascribed to  
 182 secondary amine ( $-\text{NH}$ ) of the SHz moiety ( $398.5 \text{ eV}$ ),  
 183 imine-N ( $399.1 \text{ eV}$ ) of the newly formed COF networks, and  
 184 imine-N ( $401.7 \text{ eV}$ ) of the SHz moiety.<sup>41</sup> The C nuclei with  
 185 different environments were investigated by a deconvoluted  
 186 high-resolution C 1s XPS scan (Figure 3b). The major  
 187 component at  $284.7 \text{ eV}$  is attributed to the aromatic  $\text{sp}^2 \text{ C}$   
 188 atom. Another component at  $285.2 \text{ eV}$  can be assigned to the  
 189 N atom associated with imine linkage. The peak at a higher  
 190 binding energy ( $287.8 \text{ eV}$ ) is probably due to thiadiazolic C of  
 191 the COF. Strong characteristic S 2p doublet peaks (Figure 3d)  
 192 were observed at  $163.8 \text{ (S 2p3/2)}$  and  $168.6 \text{ eV (S 2p1/2)}$ .<sup>43</sup>  
 193

The thermal stability of the covalent framework was  
 194 estimated by using thermogravimetric analysis (TGA) under  
 195 the aerobic environment. As seen from Figure S8 (Supporting  
 196 Information), an initial weight loss could be assigned to the  
 197 trapped guest molecule in the porous framework. Then, with  
 198 the continuous increase in temperature, the organic framework  
 199 is stable up to  $350 \text{ }^\circ\text{C}$ . With a further increase in temperature,  
 200 a continuous weight loss is associated with the burning of  
 201 organics present in the material. The representative FESEM  
 202 (Figure 4a) and HRTEM (Figure 4b) images of the as-  
 203 synthesized thiadiazole COF have clearly shown regularly their  
 204 spherical morphology with diameters of  $0.5\text{--}0.8 \text{ }\mu\text{m}$ . After the  
 205 supercritical  $\text{CO}_2$  activation, it was observed that the smooth  
 206 spherical surface of the as-synthesized COF material trans-  
 207 formed to the microflower-shaped structure (Figure 4c–f)  
 208 with the size distribution of  $1.2\text{--}1.8 \text{ }\mu\text{m}$ . This is also reflected  
 209 by the nitrogen sorption isotherm with enhancing the BET  
 210 surface area (Figure S4).  
 211

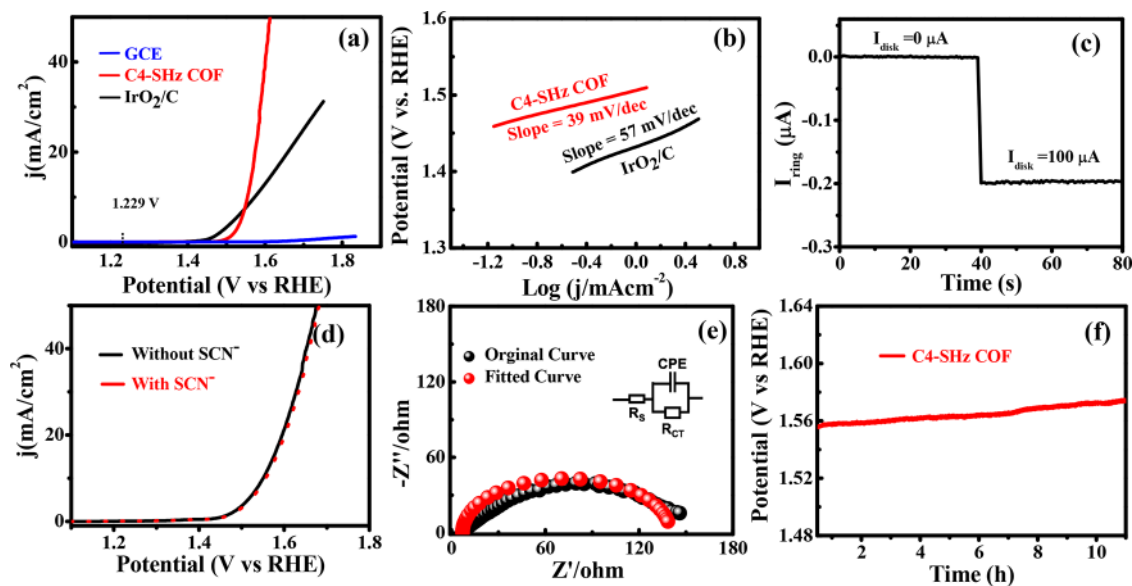


**Figure 4.** FESEM micrographs of the (a) as-synthesized and (c, d) crystalline C4-SHz COF. Representative TEM images of the (b) as-synthesized and (e, f) crystalline C4-SHz COF material.

To determine the electrocatalytic OER activity of the as-synthesized catalyst, linear sweep voltammetry (LSV) was recorded. The OER activity of the C4-SHz COF was compared with the state-of-the-art catalyst IrO<sub>2</sub>/C and bare GCE under similar conditions. Before the LSV measurement,

the C4-SHz COF catalyst was electrochemically preconditioned to reach a stable state (Figure S9, Supporting Information). All the LSV plots are presented after *iR* compensation. The *iR* compensation process is explained in the Supporting Information (Figure S10). Figure 5a presents the *iR*-compensated LSV polarization plots. As expected, the bare glassy carbon electrode (GCE) exhibits a very low anodic current density with higher overpotential values, suggesting its negligible OER activity. The C4-SHz COF-modified GCE shows a sharp increase in the anodic current density, which indicates its intrinsic OER activity. For electrocatalytic activity, the overpotential ( $\eta$ ) gives an idea about the extent of polarization upon passage of the faradic current and reflects the efficiency of the catalysts. The catalyst C4-SHz COF possesses the higher activity with a lower onset overpotential of 250 mV, which is higher than that of benchmark catalyst IrO<sub>2</sub>/C. The current density of 10 mA/cm<sup>2</sup> is the critical value for driving solar fuel conversion and used as a benchmark for comparing electrocatalytic performance. The as-synthesized C4-SHz COF achieved a current density of 10 mA/cm<sup>2</sup> at a lower overpotential of 320 mV, which is lower than benchmark catalyst IrO<sub>2</sub>/C. The overpotential of the C4-SHz COF is comparable with most of the reported metal-free OER electrocatalysis (Table S3, Supporting Information). This result suggests the promising electrocatalytic activity of the highly crystalline C4-SHz COF toward the OER. The OER activity is also compared with a moderately crystalline C4-SHz COF. The highly crystalline C4-SHz COF exhibits a lower overpotential with enhanced current density in comparison to moderately crystalline C4-SHz COF (Figure S11, Supporting Information). Further, the OER activity of the highly crystalline C4-SHz COF is checked in different conditions, i.e., acidic (0.5 M H<sub>2</sub>SO<sub>4</sub>) and neutral (1 M PBS) solutions. The C4-SHz COF exhibits the higher OER activity in 1 M KOH (Figure S12, Supporting Information).

The reaction dynamics and mechanism of the as-synthesized catalysts toward the OER were investigated by measuring the



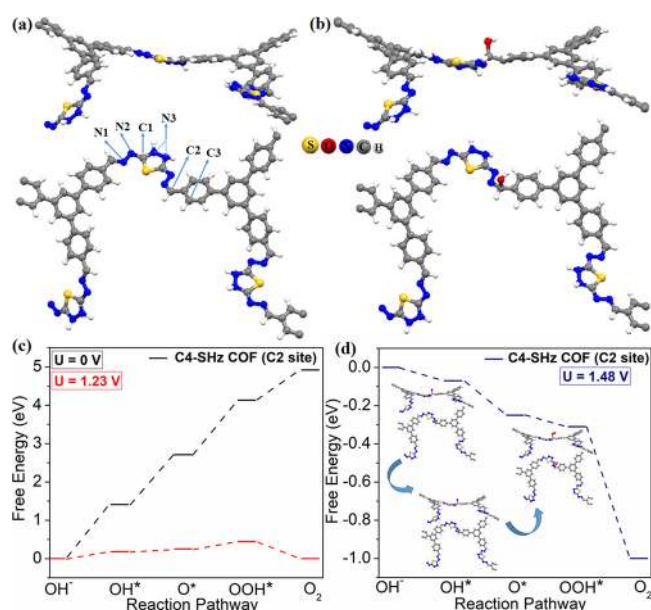
**Figure 5.** OER performance of the catalysts in 1 M KOH with a scan rate of 5 mV/s. (a) LSV polarization plots of the C4-SHz COF, IrO<sub>2</sub>/C, and GCE. (b) Tafel plots of the C4-SHz COF and IrO<sub>2</sub>/C. (c) Faradic efficiency calculation of the C4-SHz COF by using the RRDE technique. (d) LSV polarization plot of the C4-SHz COF before and after the addition of 10 mM KSCN. (e) EIS Nyquist plot for the C4-SHz COF. (f) Chronopotentiometry measurement shows the stability of C4-SHz COF.

254 Tafel slope from Tafel plots. The Tafel plots are obtained from  
255 the LSV measurements and reflect the relationship between  
256 the overpotential ( $\eta$ ) and the log of current density. The Tafel  
257 slope is derived from the linear part of the Tafel plot, and lower  
258 the Tafel slope value indicates the higher electrocatalytic  
259 activity. The C4-SHz COF exhibits the lower Tafel slope of 39  
260 mV/dec, which is lower than that for IrO<sub>2</sub>/C (57 mV/dec)  
261 (Figure S**5b**). The Tafel slope of the C4-SHz COF is lower than  
262 that of other reported metal-free catalysts. The exchange  
263 current density ( $j_0$ ) of the C4-SHz COF is calculated from the  
264 Tafel plot by the extrapolation method (Figure S**13**,  
265 Supporting Information). The exchange current density ( $j_0$ )  
266 of the C4-SHz COF is estimated to be  $3.95 \times 10^{-4}$  mA/cm<sup>2</sup>.  
267 The value of  $j_0$  is also proportional to the electrochemically  
268 active surface area. The small Tafel slope and large exchange  
269 current density indicate that the C4-SHz COF can produce  
270 superior metal-free OER performance. The faradic efficiency  
271 (FE) of the catalysts is measured by the rotating ring-disk  
272 electrode (RRDE) experiment.<sup>44,45</sup> The RRDE experimental  
273 details are discussed in the Supporting Information. The FE is  
274 calculated from the ratio of the ring current to the disk current  
275 (eq S**3**, Supporting Information). A constant current of 100  $\mu$ A  
276 is applied to the disk electrode, and a 19.6  $\mu$ A current was  
277 generated at the ring electrode (Figure S**5c**), which corresponds  
278 to the promising FE of the C4-SHz COF (98%). The  
279 formation of the oxygen bubble during the OER was supported  
280 by the polarization curve of the oxygen reduction reaction  
281 (ORR) collected from the ring electrode at a constant disk  
282 potential of 1.50 V (Figure S**14a**, Supporting Information).  
283 The number of electron transfer during the OER was also  
284 calculated from the RRDE measurement. During OER  
285 polarization, a very negligible current density was observed  
286 in the ring electrode that is assigned to the electro-oxidation of  
287 generated H<sub>2</sub>O<sub>2</sub> (Figure S**14b**). This observation validates the  
288 four-electron pathway for the OER.

289 Generally, the precursor used for the synthesis of the COF  
290 or the electrolyte used for testing the electrocatalytic activity  
291 contains some metal catalysts (i.e., Fe<sup>3+</sup>), and it may contribute  
292 toward the OER activity of the as-synthesized materials. To  
293 rule out the contribution of metal ions (i.e., Fe<sup>3+</sup>), SCN<sup>-</sup> tests  
294 were carried out. The LSV data of the C4-SHz COF is  
295 collected before and after the addition of the SCN<sup>-</sup> ions, and it  
296 suggests that SCN<sup>-</sup> ions did not affect the OER activity, i.e.,  
297 the OER activity is due to the metal-free C4-SHz COF catalyst  
298 (Figure S**5d**). This suggests that both the C4-SHz COF and  
299 electrolyte (KOH) are free from metal impurities.<sup>14</sup> The  
300 enhanced catalytic activity of the C4-SHz COF was further  
301 accessed by calculating active sites and the intrinsic catalytic  
302 activity. Therefore, we explored the mass activity, specific  
303 activity, electrochemically active surface area (ECSA), and  
304 roughness factor ( $R_f$ ) of C4-SHz COF catalysts. At  $\eta = 320$   
305 mV, the mass activity and specific activity for the C4-SHz COF  
306 catalyst were found to be 286 A g<sup>-1</sup> and 0.011 mA/cm<sup>2</sup>,  
307 respectively. To measure the electrochemically active surface  
308 area (ECSA) and roughness factor, electrical double layer  
309 capacitance (Cdl) of the C4-SHz COF was evaluated by  
310 measuring the CV in the non-faradic region at scan rates of  
311 10–100 mV/s in 1 M KOH at a potential ranging from 0 to  
312 0.1 V (Ag/AgCl) and is shown in Figure S**15a**, Supporting  
313 Information. The value of Cdl is estimated from the linear  
314 slope and found to be 2.75 mF cm<sup>-2</sup> (Figure S**15b**, Supporting  
315 Information). The ECSA and  $R_f$  values of the C4-SHz COF  
316 were estimated to be 68.75 cm<sup>2</sup> and 968.30, respectively. Thus,

the C4-SHz COF shows a high electrochemical catalytic 317  
surface area that may be due to the exposed excess nitrogen 318  
atom on the surface, which plays as the active sites for the OER 319  
activity. The high surface area and the porous structure can 320  
facilitate the diffusion of the electrolyte to access more number 321  
of reactant species on the electrode surface that resulted in an 322  
enhanced performance during the OER. The high mass and 323  
specific activity of the C4-SHz COF may also be associated 324  
with fast charge transfer during the OER process. The 325  
electrochemical impedance spectroscopic (EIS) Nyquist plot 326  
of the C4-SHz COF is also presented in Figure S**5e**. The smaller 327  
polarization resistance of the C4-SHz COF indicates the higher 328  
charge transfer kinetics and faster electron transfer process that 329  
supports the OER activity.<sup>46</sup> The durability is another key 330  
factor to evaluate the catalytic activity in practical application. 331  
The long-term durability of the C4-SHz COF has been studied 332  
by chronopotentiometry measurements. The time-dependent 333  
chronopotentiometry measurements demonstrate that the C4- 334  
SHz COF is a stable material and can work efficiently for more 335  
than 11 h at a current density of 10 mA/cm<sup>2</sup> (Figure S**5f**). 336  
Further, the stability of the C4-SHz COF at higher current 337  
densities (20 and 50 mA/cm<sup>2</sup>) has been checked with time- 338  
dependent chronopotentiometry measurement (Figure S**16**, 339  
Supporting Information). The as-synthesized material shows a 340  
quite stable response at higher current densities as well. The 341  
above measurements demonstrate the enhanced efficiency and 342  
robustness of the C4-SHz COF toward the OER and validate 343  
its promising application in future energy devices. It is quite 344  
essential to understand the structure, morphology, and any 345  
alternation of the bonding connectivity of the C4-SHz COF 346  
after the durability test. The post-OER analysis validates the 347  
robust properties of the electrocatalyst for practical application. 348  
Therefore, PXRD and FTIR analyses have been carried out 349  
after the stability test. In the PXRD patterns, no change in the 350  
crystal phase was observed (Figure S**17**, Supporting 351  
Information). This result suggested the stability of the 352  
crystalline COF structure in the electrocatalyst. FTIR spectra 353  
confirm the retention of the bonding connectivity within the 354  
organic framework (Figure S**18**, Supporting Information) after 355  
the OER stability test, suggesting the C4-SHz COF as a robust 356  
material. 357

The mechanism of the OER process and the efficiency of the 358  
C4-SHz COF material toward the electrochemical OER are 359  
rationalized through a density functional theory study based on 360  
first-principle calculations using the VASP simulation package. 361  
We have constructed a periodic monolayer model of C4-SHz o 362  
(cell size: 31.09  $\times$  27.22  $\text{\AA}^2$ ) consisting of 123 atoms, as shown 363  
in Figure 6a. The efficiency of the OER can be determined by 364  
calculating the reaction free energies of the individual 365  
elementary steps.<sup>47</sup> Therefore, the free-energy change for the 366  
adsorption of the intermediates (i.e., OH\*, O\*, and OOH\*) 367  
on the C4-SHz surface has been calculated, and free-energy 368  
profiles for OER pathways at  $U = 0$  and 1.23 V are given in 369  
Figure 6c. For OH<sup>-</sup> adsorption on the C4-SHz surface, there 370  
are seven possible sites, including the S atom (Figure 6b and 371  
Figure S**19**, Supporting Information). However, adsorption of 372  
OH<sup>-</sup> is more favorable on the C2 site with the highest OH<sup>-</sup> 373  
adsorption energy of -1.61 eV (Figure 6b and Table S**4**). 374  
However, there are very weak interactions between OH<sup>-</sup> and 375  
either the N3 or S site (Figure S**19e,f**). Therefore, the active 376  
site for OH<sup>-</sup> adsorption is predominantly the C2 site. From 377  
the free-energy profile diagram (Figure 6c), it is evident that 378  
OOH\* adsorption with the highest (most positive) free-energy 379



**Figure 6.** (a) Theoretically optimized structure of the C4-SHz monolayer (different C and N sites are marked) and (b) most stable structure of the OH\* adsorbed C4-SHz surface (all other possible OH<sup>-</sup> adsorption sites are shown in Figure S19, Supporting Information). (c) Free-energy profile for the OER pathway in alkaline medium on the C2 site at  $U = 0$  and 1.23 V for the C4-SHz COF. (d) Free-energy profile at the experimentally determined onset potential, i.e., at an applied bias of  $U = 1.48$  V (inset shows the structures of adsorption intermediates OH\*, O\*, and OOH\* on the C2 site of the C4-SHz surface).

380 value is the rate-determining step during the OER process for  
381 the C4-SHz COF.<sup>47</sup>

382 The free-energy values of OOH\* adsorption on the C4-SHz  
383 surface are 4.13 and 0.44 eV at  $U = 0$  and 1.23 V. This finding  
384 is consistent with the earlier reported COF material as the  
385 metal-free OER electrocatalyst.<sup>33</sup> To get further insight about  
386 the excellent electrocatalytic activity of the C4-SHz COF, we  
387 have performed density of states (DOS) analysis. Total and  
388 projected density of states (TDOS and PDOS) analysis clearly  
389 demonstrates that the VBM is mainly composed of the 2p  
390 orbital of C atoms, whereas the 2p orbitals of heteroatoms, i.e.,  
391 N and S atoms, contribute to the CBM (Figure S20,  
392 Supporting Information). Among various C sites, as evident  
393 from Figure S20b, the major contribution to the VBM comes  
394 from the C2 sites. Therefore, upon adsorption of energy, holes  
395 will be generated mainly on C atoms (especially on the C2  
396 atom), and heteroatom sites will be electron-rich. For the OER  
397 process in alkaline medium, OH<sup>-</sup> is oxidized to O<sub>2</sub> after  
398 absorbing holes from the active C2 sites, which is consistent  
399 with previously reported COFs and heteroatom-doped  
400 graphene systems.<sup>33,48,49</sup> Besides, we have determined the  
401 free-energy profile for the OER pathway at an applied bias of  
402 1.48 V (Figure 6d), which is the experimentally determined  
403 onset potential. Interestingly, the energy profile diagram  
404 exhibits the downhill OER pathway at  $U = 1.48$  V, validating  
405 the experimental findings of the OER onset overpotential.  
406 Moreover, the downhill OER pathway at  $U = 1.48$  V also  
407 indicates that the lower overpotential (merely 250 mV) arises  
408 due to the C2 active site on the surface.<sup>33</sup>

## CONCLUSIONS

409

In summary, we have fabricated a novel thiadiazole-based  
410 covalent organic framework, C4-SHz COF, through the Schiff  
411 base condensation polymerization reaction between 1,3,5-  
412 tris(4-formylphenyl)benzene and 2,5-dihydrazinyl-1,3,4-thia-  
413 diazole under vacuum in a sealed tube. The resultant material  
414 displayed a unique molecular architecture, high porosity, BET  
415 surface area, and accessible active sites, which could enable this  
416 COF as a superior self-supported metal-free OER electro-  
417 catalyst. In the alkaline system, the material showed a low  
418 onset potential of 270 mV, and the material achieved a current  
419 density of 10 mA/cm<sup>2</sup> with a lower overpotential of 320 mV.  
420 The accomplished OER activity is comparable to other best  
421 reported metal-free catalysts with excellent durability. There-  
422 fore, the catalytic performance exhibited by C4-SHz COF  
423 suggests that it may replace metal-free carbon-based nanoma-  
424 terials and could be a promising electrocatalyst for future  
425 energy conversion from abundant water resources. 426

## ASSOCIATED CONTENT

427

### Supporting Information

428

The Supporting Information is available free of charge at  
429 <https://pubs.acs.org/doi/10.1021/acscatal.9b05470>. 430

Materials, methods and characterization tools, exper-  
431 imental details, Pawley refined powder X-ray profile with  
432 other related data, simulated N<sub>2</sub> adsorption isotherm,  
433 TGA profile, comparison table with other reported  
434 catalysts, CV plot of materials before LSV measurement,  
435 *i*R-corrected LSV curve, exchange current density plot,  
436 RRDE measurement plot, ECSA plot, stability at  
437 different density plot, PXRD and FTIR of used COF  
438 materials, and computational OER mechanism related  
439 data (PDF) 440

(PDF) 441

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#### 477 Notes

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