Supporting information for

Carbon derived from soft pyrolysis of COF as a support for small-sized RuO$_2$ showing exceptionally low-overpotential for OER

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1. Material and Methods:

Scheme S1. Schematic representation of IISERP-COF1 and IISERP-COF6.
Table S1. Comparative table for the OER performances with recently reported catalysts:

| S. No | Material                          | Electrolyte | Overpotential (mV) | Reference                  |
|-------|-----------------------------------|-------------|--------------------|----------------------------|
| 1     | Fe(PO₃)₂/Ni₃P                     | 1 M KOH     | 177 @ 10 mA/cm²    | PNAS, 2017, 114, 5607.     |
| 2     | Gelled FeCoW oxy-hydroxide        | 0.1 M KOH   | 191 @ 10 mA/cm²    | Science 2016, 10.1126/science.aaf1525. |
| 3     | FeNi-rGO LDH                      | 1 M KOH     | 195 @ 10 mA/cm²    | Angew. Chem. Int. Ed., 2014, 53, 7584. |
| 4     | FeNi-GO LDH                       | 1 M KOH     | 210 @ 10 mA/cm²    | Angew. Chem. Int. Ed., 2014, 53, 7584. |
| 5     | IISERP-COF1_RuO₂@370              | 1 M KOH     | 210 @ 10 mA/cm²    | This Work.                  |
| 6     | IISERP-COF6_RuO₂@350              | 1 M KOH     | 217 @ 10 mA/cm²    | This Work.                  |
| 7     | IISERP-COF3_Ni₃N                  | 1 M KOH     | 230 @ 10 mA/cm²    | Adv. Energy Mater., 2016, 6, 1601189. |
| 8     | RuO₂                              | 0.5 M H₂SO₄ | 240 @ 1 mA/cm³     | Electrochim. Acta, 1998, 44, 1515. |
| 9     | IISERP-COF2 Nanocomposite         | 0.1 M KOH   | 258 @ 10 mA/cm²    | Adv. Energy Mater., 2016, 6, 1600110 |
| 10    | 1D-RuO₂-CNx                       | 0.5 M KOH   | 260 @ 10 mA/cm²    | ACS Appl. Mater. Interf., 2016, 8, 28678. |
| 11    | CoO₀@CN                           | 1 M KOH     | 260 @ 10 mA/cm²    | J. Am. Chem. Soc., 2015, 137, 2688–2694 |
| 12    | IrO₂                              | 0.5 M H₂SO₄ | 270 @ 1 mA/cm³     | Chem. Soc. Rev., 2017, 46, 337. |
| 13    | RuO₂                              | 1 M NaOH    | 275 @ 10 mA/cm³    | ACS Catal., 2016, 6, 2408.    |
| 14    | IrO₂                              | 0.5 M H₂SO₄ | 276 @ 1 mA/cm³     | Electrochim. Acta, 1998, 44, 1515. |
| 15    | RuO₂                              | 1 M KOH     | 290 @ 10 mA/cm²    | ACS Appl. Mater. Interf., 2016, 8, 4718. |
| 16    | RuO₂/TM                           | 1 M KOH     | 290 @ 10 mA/cm²    | Nanotechnology, 2016, 27, 23LT01. |
| 17    | α-Co₃O₄Fe(OH)₆ nanosheet           | 1 M KOH     | 295 @ 10 mA/cm²    | J. Mater. Chem. A, 2017, 5, 1078–1084. |
| 18    | NiSe₂/Ti                          | 1 M KOH     | 295 @ 20 mA/cm²    | ACS Appl. Mater. Interf., 2016, 8, 4718. |
| 19    | NiFe-LDH                          | 1 M KOH     | 300 @ 10 mA/cm²    | Nat. Commun., 2014, 5, 4477. |
| 20    | RuO₂/C                            | 0.1 M KOH   | 310 @ 10 mA/cm²    | ACS Catal., 2017, 7, 819–832  |
| 21    | RuO₂/Au                           | 1 M NaOH    | 320 @ 10 mA/cm²    | J. Mater. Res., 2016, 31, 18.  |
| 22    | RuO₂                              | 1 M KOH     | 325 @ 10 mA/cm²    | Small, 2017, 1604103.        |
| 23    | Co₃Fe₃O₈/CNT                      | 1 M KOH     | 326 @ 10 mA/cm³    | Small, 2016, 12, 2866.       |
| 24    | Commercial RuO₂                    | 0.5 M KOH   | 330 @ 10 mA/cm³    | ACS Appl. Mater. Interf., 2016, 8, 28678. |
| 25    | RuO₂                              | 1 M KOH     | 331 @ 10 mA/cm²    | RSC Adv., 2016, 6, 50017.    |
| 26    | RuO₂                              | 1 M KOH     | 350 @ 10 mA/cm²    | ACS Catal., 2017, 7, 103.    |
| 27    | RuO₂                              | 0.5 M KOH   | 358 @ 10 mA/cm²    | Chem. Soc. Rev., 2017, 46, 337. |
| 28    | RuO₂                              | 1 M KOH     | 360 @ 10 mA/cm²    | ChemElectroChem, 2014, 1, 2075. |
| 29    | RuO₂                              | 1 M KOH     | 366 @ 10 mA/cm²    | ChemElectroChem, 2016, 3, 719. |
| 30    | Ba₀.₅Sr₀.₅Co₀.₅Fe₂O₄               | 0.1 M KOH   | 370 @ 10 mA/cm³    | Science, 2011, 334, 1383.   |
| 31    | Co₉Fe₄O₁₃                         | 0.1 M KOH   | 370 @ 10 mA/cm³    | Nanoscale, 2015, 7, 8920.    |
| 32    | CaCu₃Fe₄O₁₂                         | 0.1 M KOH   | 400 @ 10 mA/cm³    | Nat. Commun., 2015, 6, 8249. |
| 33    | CuFe₄O₈                           | 0.1 M KOH   | 410 @ 10 mA/cm³    | Nanoscale, 2015, 7, 8920.    |
| 34    | IrO₂                              | 0.5 M KOH   | 411 @ 10 mA/cm³    | Chem. Soc. Rev., 2017, 46, 337. |
| 35    | RuO₂                              | 0.1 M KOH   | 420 @ 10 mA/cm³    | ACS Appl. Mater. Interf., 2015, 7, 12930. |
| 36    | RuO₂                              | 0.1 M KOH   | 425 @ 10 mA/cm³    | Adv. Mater., 2017, 1606793.  |
| 37    | NiFe₂O₄                           | 0.1 M KOH   | 440 @ 10 mA/cm³    | Nanoscale, 2015, 7, 8920–8930. |
| 38    | RuO₂                              | 1 M KOH     | 450 @ 10 mA/cm³    | Chem. Commun., 2014, 50, 13019. |
| 39    | MnFe₂O₄                           | 0.1 M KOH   | 470 @ 10 mA/cm³    | Nanoscale, 2015, 7, 8920.  |
**Structure solution and modelling details:**

A structure consistent with the experimentally observed powder pattern has been obtained using a combination of crystal building simulations, Pawley refinements and Density Functional Theory (DFT) based geometry optimizations carried out using the Accelrys program (Materials Studio V.6.0). In brief, the powder XRD was indexed using an X-Cell program. Following this, a space group search was executed, which suggested P6/m, P6, R3 and P3C1 as the probable ones as determined by their high figure of merit values (> 120). A crystal building was carried out in the highest symmetry among them namely the P6/m setting with the unit cell values shown in the Table S1. The structures of eclipsed and staggered were geometry optimized using the tight binding DFT routine (DFTB). The lowest energy configuration was that of the eclipsed structure. It has lower relative energy compared to the staggered form (Relative energy: -181.3 (eclipsed) vs. -100.05 kcal/mol (staggered)). Importantly, the pore sizes estimated for the eclipsed model fits the experimentally determined pore sizes much better. Hence, the eclipsed configuration with an AAA... stacking was used as the better-fitting model.

A comparison of the simulated powder XRD (PXRD) pattern of the eclipsed and the staggered models with the experimental PXRD showed that the relative intensities of the second and third most intense peaks, (110) and (200), and the peaks in the 2θ range of 13° to 17° fitted the experimentally observed relative intensities much better (Figure S1). Hence the Pawley refinements were carried out using the eclipsed model in the P6/m space group. An excellent fit was obtained (Rp = 3.77%; wRp = 5.1%). The unit cell and the atomic coordinates of the refined structure is presented in the table S2.

For the geometry optimizations of the periodic COF structures, dispersion corrected tight-binding Density Functional Theory was utilized. The Smart algorithm was used with the force fields chosen from the Slater-Koster library. The Divide and conquer eigen solver and the self-consistent charges with a SCC tolerance of $1 \times 10^{-8}$ were exercised. UFF-based Lennard-Jones dispersion corrections were included in Energy, Force and Displacement calculations and the cell were optimized. Thermal smearing with a smearing parameter of 0.005 Ha was applied. The geometry optimizations were carried out both using the unit cell as well as a $2 \times 2 \times 2$ supercell and the difference in relative energies remained the same between the eclipsed and staggered configurations. No constraints were placed on the structure during the optimizations. In all cases, excellent convergence was achieved in less than 500 SCC cycles.
**Figure S1.** Comparison of the PXRD patterns, simulated vs. experimental.

**Table S2.** Atomic coordinates of the IISERP-COF6.
Space group: P6/m; Crystal system: Hexagonal
Unit cell parameters: \(a = b = 31.395\); c = 3.3862; \(\alpha = \beta = 90\); \(\gamma = 120\).

| Atom | x     | y     | z    |
|------|-------|-------|------|
| C1   | 0.44443| 0.64958| 0.50000|
| C2   | 0.41617| 0.59836| 0.50000|
| C3   | 0.43892| 0.57018| 0.50000|
| C4   | 0.48998| 0.59119| 0.50000|
| C5   | 0.51803| 0.64261| 0.50000|
| C6   | 0.49589| 0.67124| 0.50000|
| C7   | 0.51322| 0.56024| 0.50000|
| C8   | 0.37812| 0.67261| 0.50000|
| N1   | 0.48621| 0.51231| 0.50000|
| N2   | 0.33981| 0.62613| 0.50000|
| O1   | 0.42609| 0.68264| 0.50000|
| H1   | 0.11363| 0.58351| 0.50000|
| H2   | 0.19214| 0.48095| 0.50000|
| H3   | 0.10194| 0.44173| 0.50000|
| H4   | 0.20345| 0.62374| 0.50000|
| H5   | 0.55462| 0.58002| 0.50000|
2. Analytical characterization:

**Figure S2.** $^{13}$C SSNMR of IISERP-COF6 Showing the corresponding peaks. * represent the spinning side bands and # represents the peaks due to terminal unreacted aldehydes. Figure shows the bands (triazine, -C=N- and the aromatic rings) corresponding the functionalities in the COF.
Figure S3. Photographic images of the COFs, intermediate precursors and the Composite-I and Composite-II.

Figure S4. A PXRD comparison of as made and RuO$_2$ loaded IISERP-COF1 prepared at different temperatures.
**Figure S5.** A PXRD comparison of as made and RuO₂ loaded IISERP-COF6 prepared at different temperatures.

**Figure S6.** A comparison of the TGA between the as-synthesized and RuO₂ loaded Phases of IISERP-COF1. All TGA's were carried out under a flow of N₂.
Figure S7. A comparison of the TGA between the as-synthesized and RuO₂ loaded phases of IISERP-COF6.
Figure S8. (A) PXRD and Raman spectra of the IISERP-COF1-derived carbon synthesized by annealing at 370°C. (B) N₂ adsorption isotherms of the COF-derived carbon. (C) SEM images of the carbon. (D) TEM image is showing lattice fringes suggesting that the carbon retains some of its crystallinity upon the soft pyrolysis. Inset figure shows the interplanar distance of the carbon.
Figure S9. (A) & (B) BET and Langmuir fits obtained from the N$_2$ 77 K adsorption isotherm of the carbon prepared at 370°C. (C) Pore size obtained from BJH fit to the desorption branch. (D) DFT (carbon spherical pore model) fit yields a hierarchical porous network of the carbon.

Figure S10. Comparison of the 77K N$_2$ isotherms of the COF derived carbon and the carbon derived from pyrolysis of Tartaric acid. Both sorption experiments were run using about 80 to 100mg of Carbon sample.
3. Microscopy studies:

Figure S11. FE SEM image of the as-made IISERP-COF1.

Figure S12. Energy Dispersive X-ray Analysis (EDAX) elemental mappings of the as-synthesized IISERP-COF1.
Figure S13. Energy Dispersive X-ray Analysis (EDAX) of the as-synthesized IISERP-COF1.

Figure S14. FE SEM image of the as-made IISERP-COF1_RuO$_2$@250.
Figure S15. Energy Dispersive X-ray Analysis (EDAX) of the as-synthesized IISERP-COF1$_1$RuO$_2$@250.

| Element | Weight % |
|---------|----------|
| C       | 58.40    |
| N       | 6.32     |
| O       | 26.20    |
| Ru      | 9.08     |
| Totals  | 100.00   |

Figure S16. Energy Dispersive X-ray Analysis (EDAX) of the as-synthesized IISERP-COF1$_1$RuO$_2$@250.
**Figure S17.** FE SEM image of the as-made IISERP-COF1\_RuO$_2$@280.

**Figure S18.** EDAX-elemental mapping of the IISERP-COF1-RuO$_2$@280.
| Element | Weight% |
|---------|---------|
| C K     | 62.15   |
| N K     | 5.68    |
| O K     | 22.61   |
| Ru L    | 9.57    |
| Totals  | 100.00  |

**Figure S19.** Energy Dispersive X-ray Analysis (EDAX) of the as-synthesized IISERP-COF1_RuO$_2$@280.

**Figure S20.** FE SEM image of the as-made IISERP-COF1_RuO$_2$@310.
Figure S21. Elemental mapping of the IISERP-COF1$_2$RuO$_2$@310.

| Element | Weight% |
|---------|---------|
| C K     | 62.81   |
| N K     | 9.45    |
| O K     | 19.70   |
| Ru L    | 8.04    |
| Totals  | 100.00  |

Figure S22. Energy Dispersive X-ray Analysis (EDAX) of the as-synthesized IISERP-COF1$_2$RuO$_2$@310.
Figure S23. FE SEM image of the as-made IISERP-COF1_RuO$_2$@370.

Figure S24. Elemental mapping of the IISERP-COF1_RuO$_2$@370.
Figure S25. EDAX spectrum of the as-synthesized IISERP-COF1_RuO$_2$@370.

Figure S26. FE SEM image of the as-made IISERP-COF6.
Figure S27. EDAX-elemental mapping of the IISERP-COF6.

| Element | Weight% |
|---------|---------|
| C K     | 74.04   |
| N K     | 4.82    |
| O K     | 21.14   |
| Totals  | 100.00  |

Figure S28. EDAX spectrum of the as-synthesized IISERP-COF6.
**Figure S29.** FE SEM image of the IISERP-COF6\_RuO$_2$@250.

**Figure S30.** EDAX-elemental mapping of the IISERP-COF6\_RuO$_2$@250.
Figure S31. EDAX spectrum of the as-synthesized IISERP-COF6_RuO₂@250.

Figure S32. FE SEM image of the as-made IISERP-COF6_RuO₂@280.
Figure S33. EDAX-elemental mapping images of the IISERP-COF6_RuO$_2$@280.

| Element | Weight% |
|---------|---------|
| C K     | 56.74   |
| N K     | 5.58    |
| O K     | 26.85   |
| Ru L    | 10.83   |
| Totals  | 100.00  |

Figure S34. EDAX spectrum of the as-synthesized IISERP-COF6_RuO$_2$@280.
Figure S35. FE SEM image of the as-made IISERP-COF6_RuO$_2$@310.

Figure S36. Elemental mapping of the IISERP-COF6_RuO$_2$@310.
| Element | Weight% |
|---------|---------|
| C K     | 46.95   |
| N K     | 16.19   |
| O K     | 28.29   |
| Ru L    | 8.57    |
| Totals  | 100.00  |

Figure S37. EDAX spectrum of the as-synthesized IISERP-COF6_RuO$_2$@310.

Figure S38. FE SEM image of as made IISERP-COF6_RuO$_2$@350.
Figure S39. Elemental mapping of the IISERP-COF6_RuO$_2$@350.

| Element | Weight% |
|---------|---------|
| C K     | 31.39   |
| N K     | 8.61    |
| O K     | 31.89   |
| Ru L    | 28.11   |
| Totals  | 100.00  |

Figure S40. EDAX spectrum of the as-synthesized IISERP-COF6_RuO$_2$@350.
Figure S41. Particle size distribution of RuO$_2$ nanoparticles in (A) carbon derived from IISERP-COF1 and (B) carbon derived from IISERP-COF6.

**IISERP-COF1$_{\text{RuO}_2}$@370**
- Average particle size: 3.13 nm
- W: 0.54 nm
- Standard deviation: $(0.54/2) = 0.27$ nm
- Average particle size with error: $3.13 \pm 0.27$ nm
- Polydispersity: $(0.27/3.13)^*100 = 8.63\%$

**IISERP-COF6$_{\text{RuO}_2}$@350**
- Average particle size: 3.42 nm
- W: 1.14 nm
- Standard deviation: $(1.14/2) = 0.57$ nm
- Average particle size with error: $3.42 \pm 0.57$ nm
- Polydispersity: $(0.57/3.42)^*100 = 16.17\%$

Figure S42. HRTEM images for IISERP-COF1$_{\text{RuO}_2}$@370 showing the lattice fringes for RuO$_2$.
Inset; SAED pattern showing poor crystallinity or in other words the particles are truly small.
Figure S43. HRTEM images for IISERP-COF6_RuO$_2$@350 showing the lattice fringes for RuO$_2$. Inset: SAED pattern showing poor crystallinity or in other words the particles are truly small.
4. Spectroscopy studies:

**Figure S44.** A comparison of the infrared spectra of the as-synthesized and RuO$_2$ loaded phases of IISERP-COF1.

**Figure S45.** A comparison of the infrared spectra of the as-synthesized and RuO$_2$ loaded phases of IISERP-COF6.
**Figure S46.** IR spectra of the IISERP-COF1$_2$RuO$_2$@370 composite show the stretching bands arising from the characteristic Ru-O and Ru-N bonds.

**Figure S47.** Raman Spectra of the COF (A) and the composite (B).
Figure S48. I-V plots from the four-probe measurement done using the IISERP-COF1_RuO₂@370. Electronic conductivity of the IISERP-COF1_RuO₂@370 was $2 \times 10^{-5}$ S/cm. This is quite decent comparing that this is a self-standing (no metal) carbonaceous material.

5. Gas sorption studies:

Figure S49. Nitrogen adsorption-desorption isotherms collected at 77K.

The 77K N₂ adsorption isotherm is of the type2 suggesting a mesoporous structure, the sharp uptake at lower pressures resembling a micropore and the lack of a prominent condensation tail at P/P₀ close to 1 indicate the pores are not too large. IISERP-COF6 shows a slightly lower uptake of N₂ compared to IISERP-COF1.
Figure S50. Pore size distribution of the as-made and the RuO₂ loaded IISERP-COF1 from BJH model. These were calculated using 77K N₂ adsorption isotherms.

Figure S51. Pore size distribution of the as-made and RuO₂ loaded IISERP-COF6 from BJH model. These were calculated using the 77K N₂ adsorption isotherms.
Figure S52. BET surface area of the IISERP-COF1 (mg scale) calculated from 77K N₂ isotherm.

Figure S53. BET surface area of the IISERP-COF1 (g scale) calculated from 77 K N₂ isotherm.
Figure S54. BET surface area of the IISERP-COF1 (water soaked) calculated from 77 K N₂ isotherm.

Figure S55. BET surface area of the IISERP-COF1 (KOH soaked) calculated from 77 K N₂ isotherm.
Figure S56. BET surface area of the IISERP-COF1_RuO₂@250 calculated from 77 K N₂ isotherm.

Figure S57. BET surface area of the IISERP-COF1_RuO₂@280 calculated from 77 K N₂ isotherm.
Figure S58. BET surface area of the IISERP-COF1_RuO$_2$@310 calculated from 77 K N$_2$ isotherm.

Figure S59. BET surface area of the IISERP-COF1_RuO$_2$@370 calculated from 77 K N$_2$ isotherm.
**Figure S60.** BET surface area of the IISERP-COF6 (mg scale) calculated from 77 K N₂ isotherm.

**Figure S61.** BET surface area of the IISERP-COF6 (g scale) calculated from 77 K N₂ isotherm.
Figure S62. BET surface area of the IISERP-COF6 (water soaked) calculated from 77 K N$_2$ isotherm.

Figure S63. BET surface area of the IISERP-COF6 (KOH soaked) calculated from 77 K N$_2$ isotherm.
Figure S64. BET surface area of the IISERP-COF6_RuO$_2$@250 calculated from 77 K N$_2$ isotherm.

Figure S65. BET surface area of the IISERP-COF6_RuO$_2$@280 calculated from 77 K N$_2$ isotherm.
Figure S66. BET surface area of the IISERP-COF6_RuO\textsubscript{2}@310 calculated from 77 K N\textsubscript{2} isotherm.
6. X-ray Photoelectron Spectroscopy (XPS):

![Figure S67. XPS spectra of IISERP-COF1_RuO₂@370. The binding energy values are calculated using fitted profiles.](image-url)
7. Electrochemical studies:

*Figure S68.* Faradaic Efficiency of the Composite-I calculated from RRDE experiment.

*Figure S69.* EDAX-elemental mapping of the IISERP-COF1_RuO$_2$@370 after OER measurements.
Table S70. EDAX of the IISERP-COF1-RuO$_2$@370 after OER measurements.
**Figure S71.** XPS spectra of the IISERP-COF1_RuO$_2$@370 after OER measurement.

**Electro Chemical Surface Area (ECSA) and roughness factor calculation for IISERP-COF1_RuO$_2$@370:**

\[ \text{C_{dl}} = 1.438 \times 10^{-5} \text{ F/cm}^2 \]
\[ \text{C}_s = 27 \mu \text{F/cm}^2 \]
\[ \text{ECSA} = \frac{\text{C}_{dl}}{\text{C}_s} = 0.532 \text{ Cm}^{-2} \]
\[ \text{RF} = \frac{\text{ECSA}}{\text{geometrical surface area of electrode}} = \frac{0.532}{0.07065} = 7.54 \]
\[ \text{TOF} = \frac{(J*A)}{4mF} \]
\[ J = \text{current density at over potential of 300 mV, } A \text{ geometrical surface area, } m = \]
\[ \text{No of moles of catalyst coated on the electrode.} \]
\[ = \frac{(0.078*0.07065)}{(4*1.386*10^{-7})*96485} \]
\[ = 0.0055107/534912.84*10^{-7} \]
\[ = 0.103 \text{ S}^{-1} \]

NOTE: Catalyst loading = 0.05 mg
Amount of Ru in 0.05 mg catalyst = 0.05*28/100 = 0.014 mg (assuming 28% Ru in the catalyst)
Amount of RuO$_2$ in 0.05 mg catalyst=0.014*133/101 =0.0184 mg
Moles of RuO$_2$ =0.0184 / (133*1000) =1.386*10$^{-7}$
Figure S72. Non-Faradaic CV of the Composite-I.

Figure S73. The plot of the anodic and the cathodic current versus the scan rate.
Table S3. Comparative table of TOF for IISERP-COF1_RuO$_2$@370 with recently reported catalysts:

| S. No. | Material                        | TOF (S$^{-1}$)        | Reference                        |
|-------|---------------------------------|-----------------------|----------------------------------|
| 1     | IISERP-COF1_RuO$_2$@370         | 0.103 at 300 mV       | This Work.                       |
| 2     | Fe(PO$_3$)$_2$/Ni$_3$P          | 0.12 at 300 mV        | PNAS, 2017, 114, 5607.           |
| 3     | Gelled FeCoW oxy-hydroxide      | 0.46 t 300 mV         | Science, 2016, 10.1126/science.aaf1525. |
| 4     | FeNi–rGO LDH                    | 0.987 at 300 mV       | Angew. Chem. Int. Ed., 2014, 53, 7584. |
| 5     | FeNi–GO LDH                     | 0.380 at 300 mV       | Angew. Chem. Int. Ed., 2014, 53, 7584. |
| 6     | IISERP-COF3 Ni$_3$N            | 0.52 at 300 mV        | Adv. Energy Mater., 2016, 6, 1601189. |
| 7     | 1D-RuO$_2$-CNx                  | 0.0961 at 350 mV      | ACS Appl. Mater. Interf., 2016, 8, 28678. |
| 8     | Commercial RuO$_2$              | 0.0250 at 350 mV      | ACS Appl. Mater. Interf., 2016, 8, 28678. |
| 9     | Ir/C                            | 0.027 at 300 mV       | Nat. Commun., 2015, 6, 6616.     |
| 10    | IISERP-COF2 Nanocomposite       | 0.0816 at 408 mV      | Adv. Energy Mater., 2016, 6, 1600110. |

Figure S74. Linear sweep voltammetry curves are showing the overpotentials for all composites prepared from Composite-II at different temperatures.
Figure S75. (A) PXRD comparisons of the RuO$_2$ supported on activated carbon vs. the COF-derived carbon. All the peaks correspond to the RuO$_2$ phase. Note that the former is more crystalline. (B) Linear sweep voltammetry curves are showing the overpotentials for the active catalysts and the RuO$_2$ doped in activated charcoal. RuO$_2$ has been encapsulated in activated charcoal by first loading Ru(acac)$_3$ in the charcoal followed by heating the composite at 350°C under air. It has been observed that the composites derived out of COF are superior than RuO$_2$/C in terms of overpotential. Also, the slightly more crystalline RuO$_2$/C has significantly higher overpotential compared to the IISERPCOF1_RuO$_2$. This suggests that a marked improvement in lowering of OER overpotential is possible from slight reduction in nanoparticle size.

**Justification on carbon derived out of COF via soft pyrolysis method:**

Forming novel carbonaceous materials from different sources is important and there is a definite advantage to producing highly structured carbons from pyrolysis of framework solids.$^{51,52}$ Small sized highly active “un-capped” RuO$_2$ nanoparticles could not be made, but for this route. COFs in some sense resemble graphene with judicially heteroatom doped in their structure. When pyrolysed, COFs produce porous carbons with hierarchical pores and the heteroatoms are more orderly doped into the carbon matrix which cannot be achieved by pyrolyzing the mixture of simple carbon precursor and nitrogen source like urea, melamine etc. The heteroatoms serve as abundant sites for catalytic processes. (Table S4) In this work, COFs generate carbons at a lower temperature retain some of its crystallinity (Figure S8) which help small-sized RuO$_2$ nano particles (~4 nm from TEM) to grow. The simple firing of the precursor does not provide porous carbon which helps in the catalytic processes.

**Table S4.** Nitrogen contents of the composites obtained from elemental analysis:

| Material                  | Nitrogen Content (%) |
|---------------------------|----------------------|
| IISERP-COF1               | 16.06                |
| IISERP-COF1_RuO$_2$@370   | 8.84                 |
| IISERP-COF6               | 20.29                |
| IISERP-COF6_RuO$_2$@350   | 7.66                 |

S1. Pachfule, P.; Shinde, D.; Majumder, M.; Xu, Q. Fabrication of carbon nanorods and graphene nanoribbons from a metal-organic framework. *Nat. Chem.* **2016**, 8, 718-724.
Discussion on the superior performance of RuO$_2$@C-370 over RuO$_2$@C-400 as a OER catalyst: From the above comparative LSV plots Figures S74 and the Figure 4D, an important discussion stems out. From the LSV measurements there is a marked jump in the onset and overpotential at a current density of 10mA/cm$^2$ between the RuO$_2$@C made at 370 vs. 400°C in the case of both the Composite-I and II. This is intriguing. The drastic drop in activity for the 400°C sample could come from either the loss of structure or the growth of RuO$_2$ into unacceptably larger particles or from change in conductivity. We investigated this using the Composite-I. We did not find any substantial difference in the conductivity or the morphology between the carbons generated at 370° or 400°C. To see the contributions from the pore-structure changes, the porosity of the carbons derived from the neat COF at 370° and 400°C were compared (Figure S76, see below). In fact, the carbon made at 400°C has better porosity. Hence, if at all the porosity was the deciding factor; the RuO$_2$@C$_{400}$ should have been the more active catalyst. But it is not the case. Interestingly, from the Figures 2C and 2I of the main text one can see that the porosity drops as the synthesis temperature is increased from 250°C to 370°C. Now, the fact that the 250°C sample does not perform as best as the 370°C sample, despite their higher porosity also means that the porosity is not only the required feature. In fact, the relatively least porous 370°C sample does perform well could mean that with the RuO$_2$ being trapped it might be providing tight binding pockets with optimal accessibility to the active sites. Whereas the more porous samples made at T < 300°C could not be having such adherence also, the nP of RuO$_2$ phase may not be sufficiently grown.

Interestingly, we notice that the peaks indicating the formation of RuO$_2$ start to appear in the PXRD only at around 370°C in the case of Composite-I (Figure S4) and at 350°C in the case of Composite-II (Figure S4 and S5). And none is observed even at 310°C. This suggests that the phase formation and the growth of the RuO$_2$ happen quite rapidly in the temperature window of 350 to 400°C. Now, comparing the PXRD pattern of the composites made at 370 and 400°C shows that the RuO$_2$ are larger in the latter (Figure S76). A Scherer fit to the peaks suggest a particle size of 8.4 nm for the RuO$_2$@C$_{370}$ and is 11.04 nm for the RuO$_2$@C$_{400}$. In comparison, the RuO$_2$ particles grow to sizes as large as 22.4 nm when the Ru(acac)$_3$ at COF is pyrolyzed at 750°C (Figure S76). Hence we can conclude that the particle size of RuO$_2$ stabilized by the COF-derived carbon is the most crucial aspect in determining the catalytic activity.

Note: The particle sizes determined from the Scherrer method are comparatively larger than what has been determined from the HRTEM images, but this is expected.$^{53}$

S3. Weibel, A.; Bouchet, R.; Boulec’h, F.; Knauth, P. The Big Problem of Small Particles: A Comparison of Methods for Determination of Particle Size in Nanocrystalline Anatase Powders. Chem. Mater. 2005, 17, 2378-2385.
Figure S76. Porosity data for IISERP-COF1 pyrolyzed at 400°C.

| Pyrolysis Temperature (°C) | FWHM (radian) | Crystallite Size (nm) |
|---------------------------|--------------|---------------------|
| 370                       | 0.0160       | 8.40                |
| 400                       | 0.0130       | 11.04               |
| 750                       | 0.0064       | 22.40               |

Figure S77. PXRD comparisons of composites pyrolyzed at different temperatures.
**Figure S78.** (A) PXRD of the IISERP-COF1$_{\text{RuO}_2}\text{@750}$ composite showing sharp peaks of the corresponding RuO$_2$ (ICDD No. 00-040-1290) indicating the growth of bigger RuO$_2$ particles in the carbon matrix. But the phase does not change. (B) LSV for the IISERP-COF1$_{\text{RuO}_2}\text{@750}$. This indicates that the smaller sized RuO$_2$ particles obtained at 350/370°C have much superior OER activity than bigger sized RuO$_2$ particles obtained at 750°C.

**Figure S79.** N$_2$ 77 K adsorption isotherm of the carbon and KOH (electrolyte) treated carbon (48hrs at RT).