

Supporting Information

Synergistic Electronic Effects in AuCo Nanoparticles Stabilized in a Triazine-based Covalent Organic Framework - Catalyst for Methyl Orange and Methylene Blue Reduction

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1. General information/remarks:

Cyanuric chloride, 4-Hydroxybenzaldehyde, gold(III) chloride trihydrate, and cobalt chloride were obtained from Sigma Aldrich. p-phenylenediamine was purchased from Avra Synthesis Pvt Ltd. All other reagents were of analytical grade. All chemicals were used without any further purification.

Powder X-ray diffraction: Powder XRDs were carried out using a Bruker D8 Advance instrument and Rigaku tabletop instrument. The data analysis was performed using the Reflex module of the Materials Studio V6.

Infrared Spectroscopy: IR spectra were obtained using a Nicolet ID5 attenuated total reflectance IR spectrometer operating at ambient temperature. The solid-state IR spectra were recorded using KBr pellets as background.

Field Emission Scanning Electron Microscopy (FESEM): FESEM images were obtained using an electron microscope equipped with an integral charge compensator and embedded EsB and AsB detectors. An Oxford Xmax instrument 80 mm² (Carl Zeiss NTS, GmbH) was integrated into electron microscope to obtain the EDAX information from the samples. Imaging conditions: 2 kV, WD= 2 mm, magnification: 200 kX, Inlens detector. For SEM images, as an initial preparation, the samples were ground thoroughly, soaked in EtOH for 30 min., and were sonicated for 2 hrs. These well-dispersed samples were drop cast on silicon wafers and dried under vacuum for at least 12 hrs.

High-Resolution Transmission Electron Microscopy (HRTEM): Transmission electron microscopy (TEM) was performed using JEM 2200FS TEM microscope, operating at an accelerating voltage of 200 kV. The diffractograms were recorded at a scanning rate of 1° min⁻¹ between 20° and 80°.

Preparation of AuCoCOF coated electrode: 5 mg of AuCoCOF was dispersed in 1 ml of EtOH and sonicated for 2 hrs. 2 µL of the dispersion was drop casted on to a CHI104 polished glassy carbon electrode with the surface area of 0.071 cm² (purchased from CH Instruments Inc.) and air-dried for an hour before performing electrochemical measurements.

Electrochemical Measurements: The cyclic voltammetry measurements were performed using the AMETEK potentiostat, in three-electrode setup mode, using VERSA STUDIO (Version 2.52) software.

In situ spectro-electrochemistry: Inside the UV cuvette, a typical three-electrode setup (Pt mesh as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode) was built and connected to the Ocean Optics instrument to observe the change of the spectra in situ. 2 mL of 40 µM aq. methyl orange was dispensed into a cuvette. 25 µL of hybrid AuCoCOF catalysts were added to it. 250 µL of freshly prepared 100 mM NaBH₄ was immediately added to the reaction mixture, and the absorbance was monitored via in-situ UV-Vis spectroscopy under applied potential with the help of a charge-discharge analyzer (CHI760, CH Instruments Inc).

2. Materials and methods for the COF synthesis and dye reduction experiments

Synthesis of the monomer: The tri-podal monomer, namely 1,3,5-triazine-2,4,6-triyl)tris(oxy))tribenzaldehyde, has been synthesized as per the previous report from our lab.^{S1}

Synthesis of IISERP-COF1: trzn-COF has been synthesized using a previously reported method^{S1} where a solvothermal reaction was performed between 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(oxy))tribenzaldehyde and benzene-1,4-diamine in 1,4 dioxane, mesitylene and aqueous acetic acid by heating at 120 °C for 72 hours. The product was isolated as a brown powder by vacuum filtration and washed with different solvents including DMF, THF, DMSO, methanol, water and acetone. This product was also subjected to a Soxhlet extraction (wash) using DMF/methanol as solvent and the filtered solid was characterized by PXRD, N₂ adsorption and IR.

Preparation of cobalt nanoparticle decorated trzn-COF: The CoCOF was synthesized by the double solvent method adopted as per the previous report from our lab^{S2}. In a typical synthesis, the COF (100 mg) was dispersed in 50 mL of n-hexane, and the mixture was stirred for about 2 hours resulting in a yellow color dispersion. To this, a clear methanolic solution of CoCl₂ hexahydrate (30 mg in 0.2 mL of MeOH (commercial grade)) was added drop by drop over a period of 3 hours with vigorous stirring. Upon addition of the methanolic metal salt solution to the COF dispersion, the solution turns from yellow to orange color. The contents were then stirred for 12 hours at room temperature. The solid particles were extracted by decanting the solvent and were dried at room temperature. The solid was heated at 100 °C for 5 hours and then cooled to room temperature. This solid was dispersed in 20 mL of water, and the reduction was carried out by adding 20 mL freshly prepared 0.6 M aqueous NaBH₄ solution under vigorous stirring. This resulting solid was washed thoroughly with deionized (DI) water and methanol. These results in the formation of the COF-supported cobalt catalysts as a blueish-brown color solid.

Preparation of gold nanoparticle decorated trzn-COF: trzn-COF (10 mg/mL) dispersed in water and sonicated for 5 mins. 1 mL of 10 mM AuCl₄.3H₂O solution and 1 mL of 10 mM HEPES buffer were dispensed to 1 mL trzn-COF solution and stirred for 30 mins at room temperature. After stirring, the solution was allowed to stand for 30 minutes in ambient and the supernatant was carefully discarded. The reaction mixture was washed with DI water (x3 times) and then DI water was added to the final reaction mixture to obtain 1 mL of the solution. The resulting hybrid COFs was stored under ambient conditions.

Preparation of mixed metal nanoparticles deposited trzn-COF: CoCOF (10 mg/mL) was dispersed in water and sonicated for 5 mins. 1 mL of 10 mM AuCl₄.3H₂O solution and 1 mL of 10 mM HEPES buffer were dispensed to 1 mL CoCOF solution and stirred for 30 mins at room temperature. After stirring, the solution was allowed to stand for 30 mins in ambient and the supernatant was carefully discarded. The reaction mixture was washed with DI water (x3 times) and then DI water is added to the final reaction mixture to obtain 1 mL of the solution. The resulting hybrid COFs were stored under ambient conditions.

Procedure for dye reduction experiments: All the glassware were rinsed in aqua regia to eliminate any contaminations from previous experiments. 2 mL of 40 μM aq. methyl orange was dispensed into an empty cuvette. 25 μL of hybrid NP-COF catalysts were then added to the cuvette. 250 μL of freshly prepared 100 mM NaBH_4 was immediately added to the reaction mixture and the reaction was monitored via in-situ UV-vis spectroscopy.

Structure solution

The structure of the COF was solved using atomic manipulation and computational crystallography using Materials Studio V6.0 (Accelrys). The detailed procedure has been described previously.^{S1}

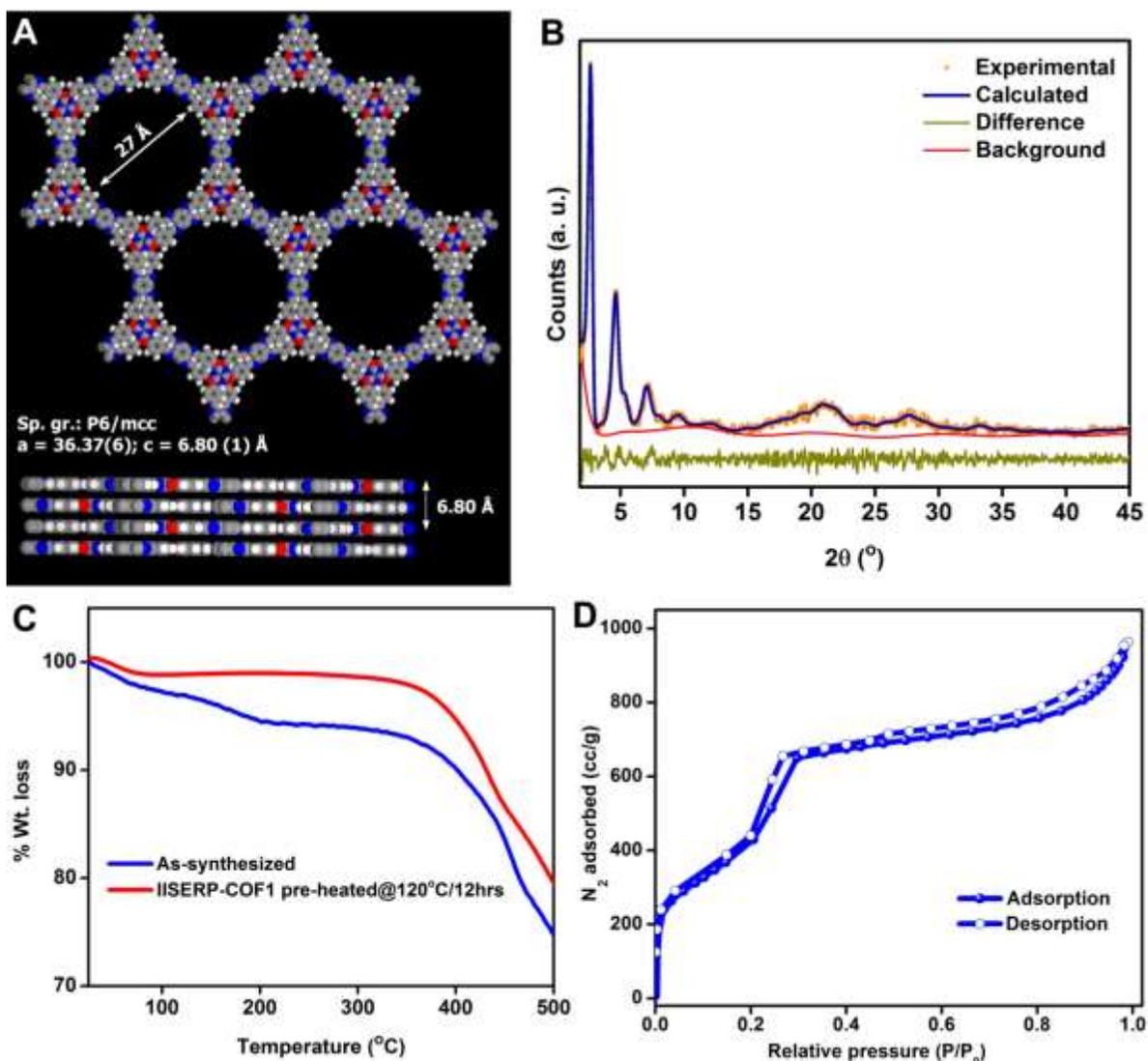


Figure S1. IISERP-COF1 characterization (A) pawley refined structure of the COF showing the large 1-D channels running along the c-direction. (B) PXRD data and Pawley fit of the COF revealing its high degree of crystallinity. (C) A comparative TGA plot of IISERP-COF1. (D) A 77K N_2 adsorption isotherm data and fit for the IISERP-COF1.

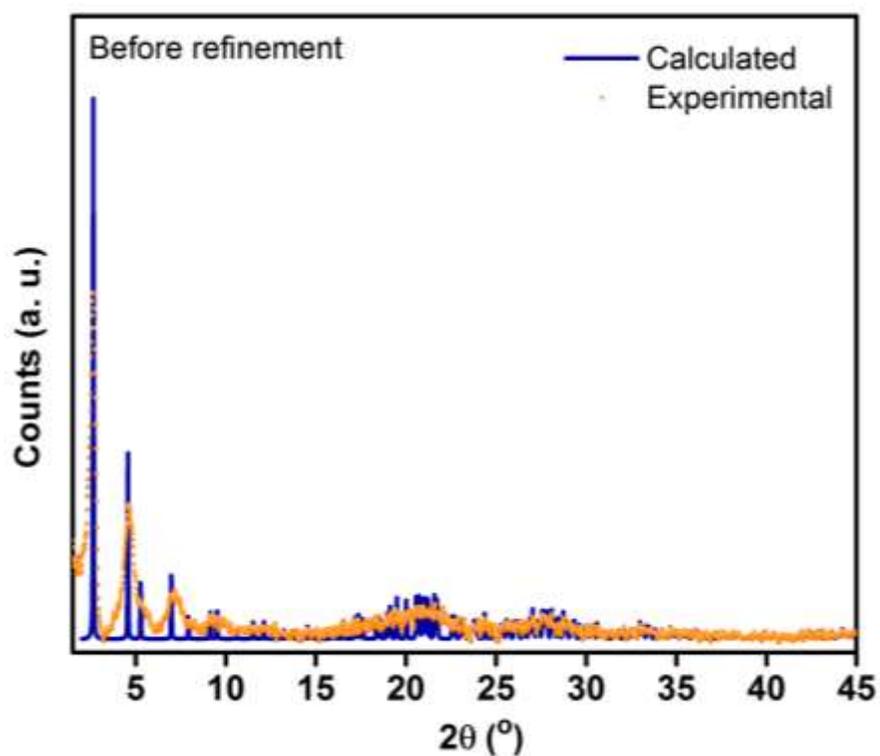


Figure S2: A comparison of the reflections from the simulated PXRD pattern of the eclipsed configuration with the experimental PXRD pattern.

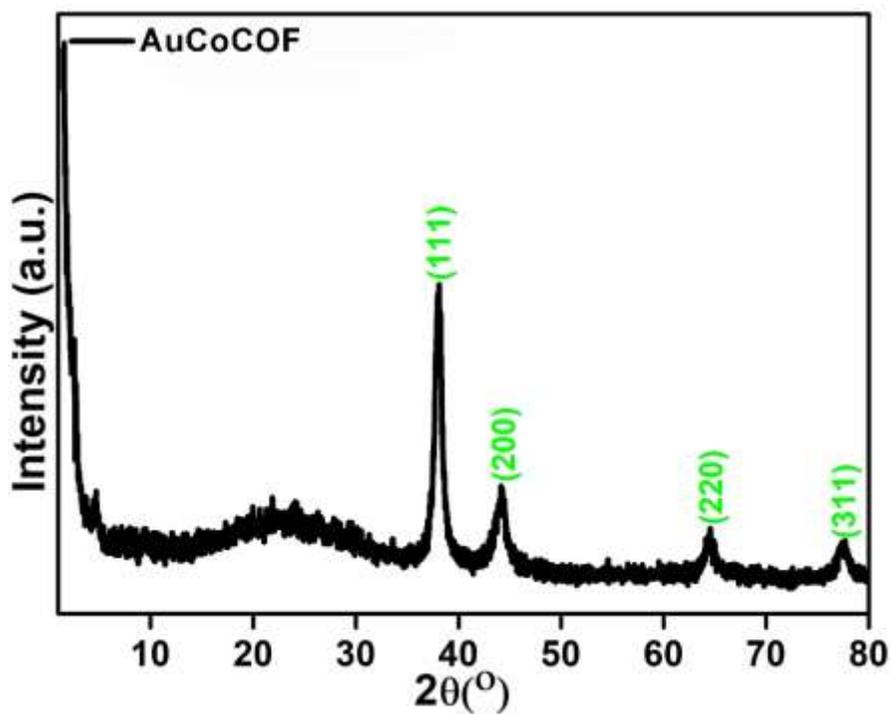


Figure S3. PXRD patterns of AuCoCOF.

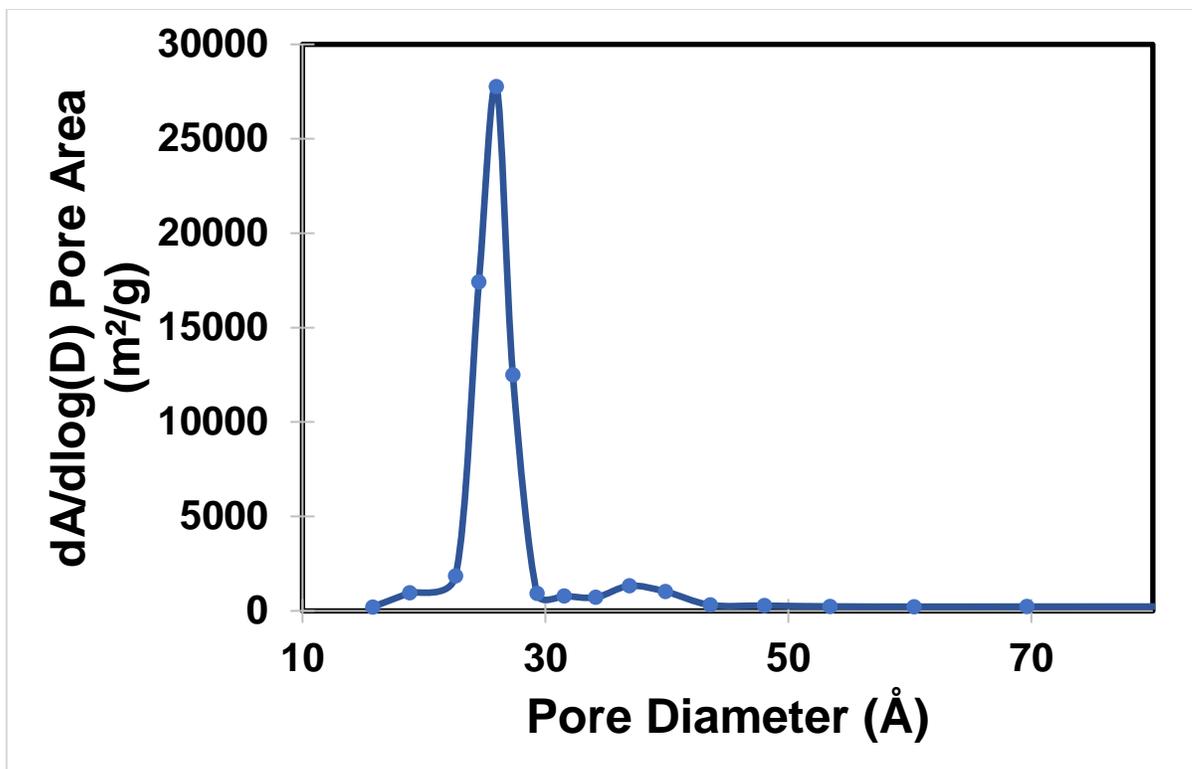


Figure S4. The pore size distribution of as-made IISERP-COF1.

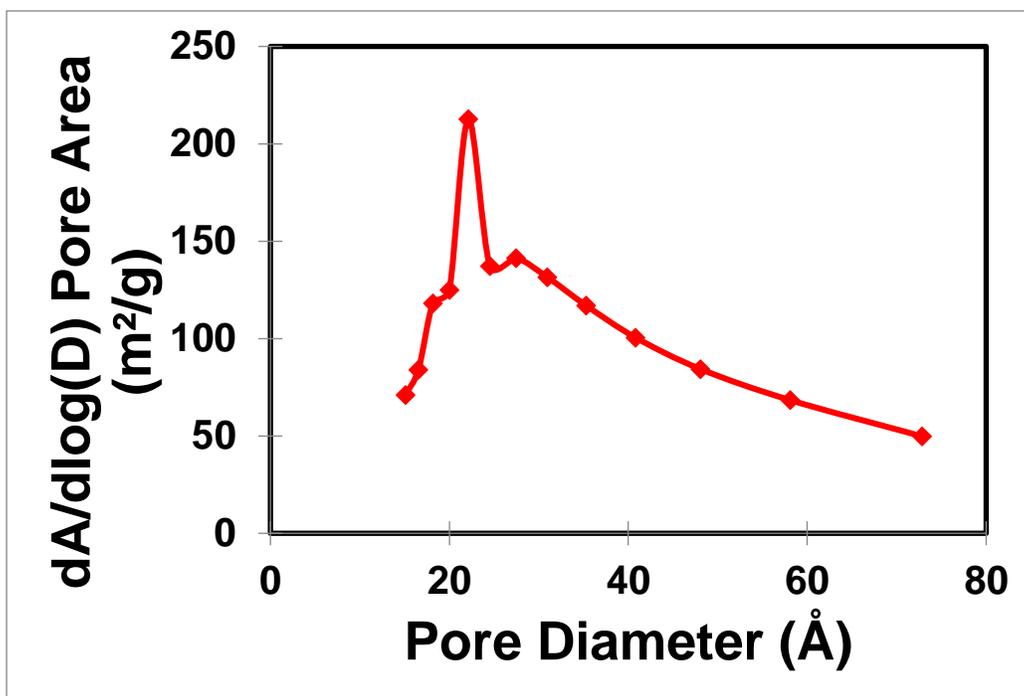


Figure S5. The pore size distribution of CoCOF. The relatively poor profile of the graph is a consequence of the substantially low gas uptake by the CoCOF composite.

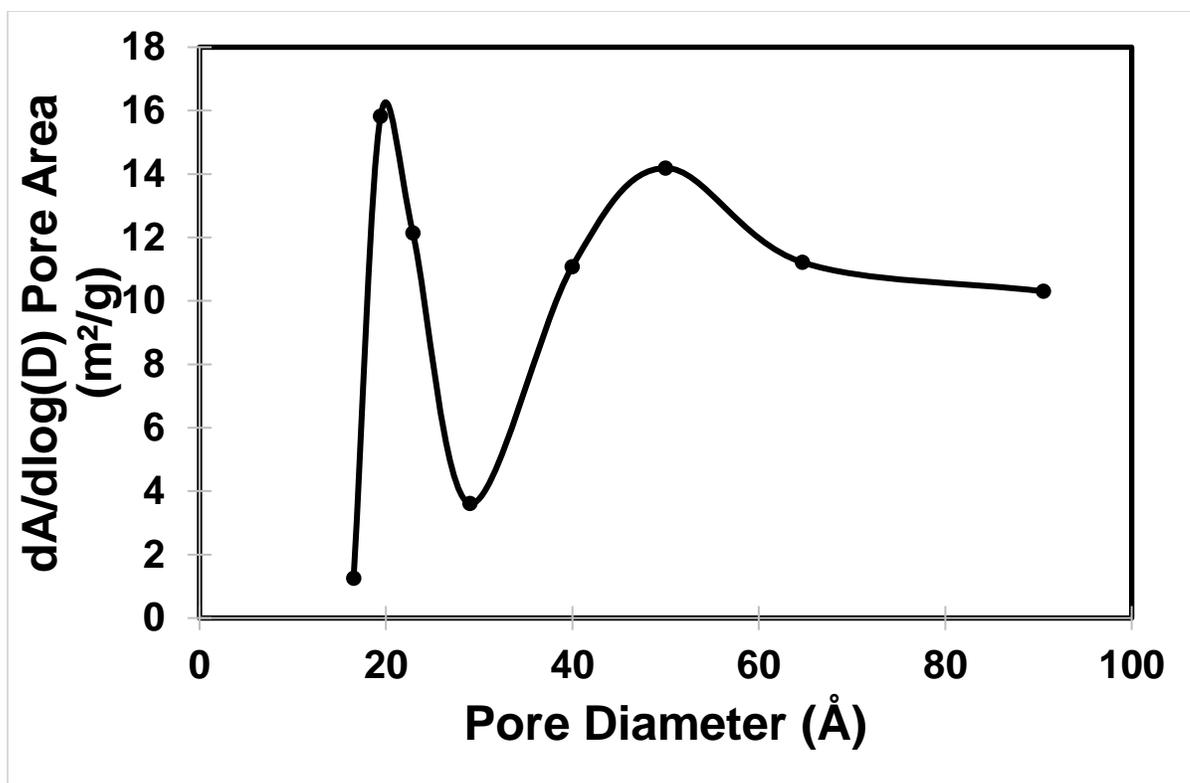


Figure S6. The pore size distribution of AuCoCOF. The relatively poor profile of the graph is a consequence of the substantially low gas uptake by the AuCoCOF composite.

Infrared Spectroscopy:

IR spectra were obtained using a Nicolet ID5 attenuated total reflectance IR spectrometer operating at ambient temperature. The background (air) was collected before the spectra acquisition of each sample.

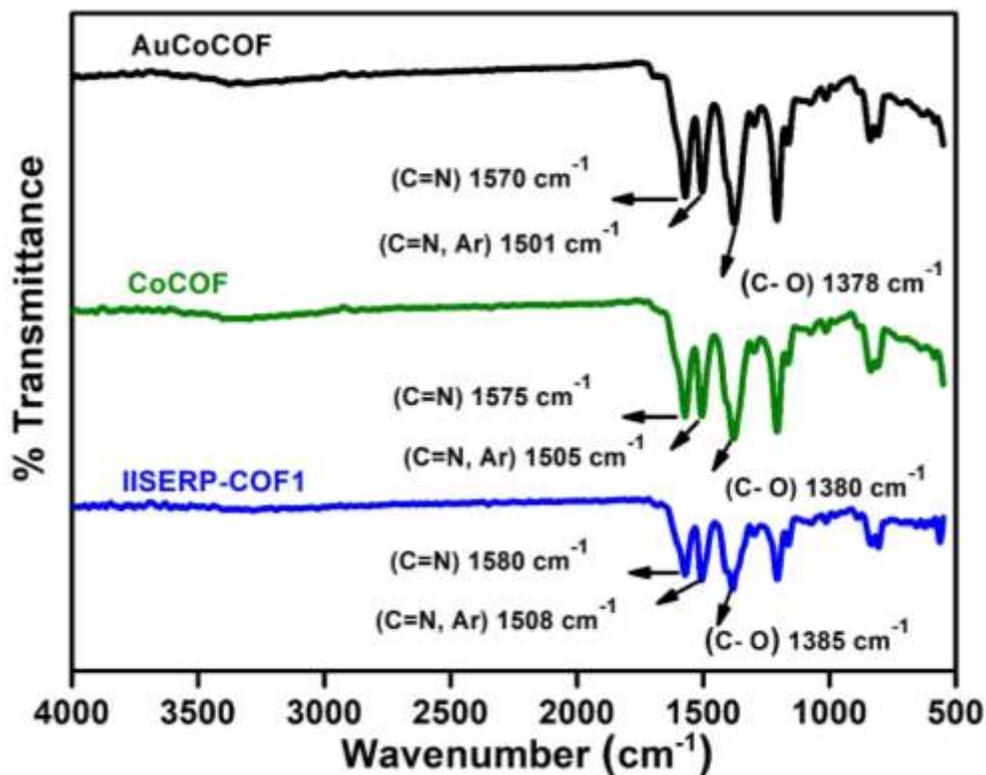


Figure S7. Comparison of the IR spectra of the as-made COF, CoCOF and AuCoCOF. Note the red-shift in the -C=N- frequency when compared between the COF vs. CoCOF and AuCoCOF, suggesting the presence of nanoparticles in the COF.

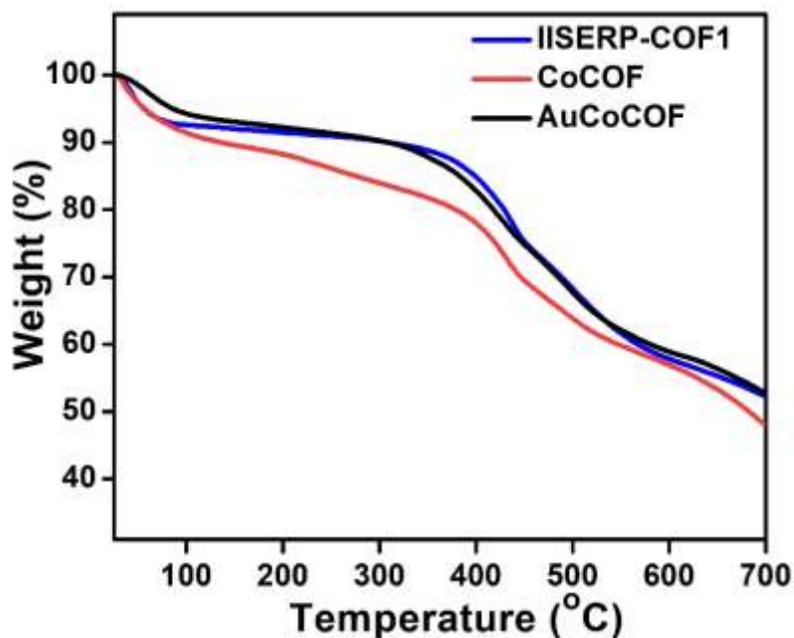


Figure S8. Comparative thermogravimetric analysis (TGA) of the as-made COF, CoCOF and AuCoCOF.

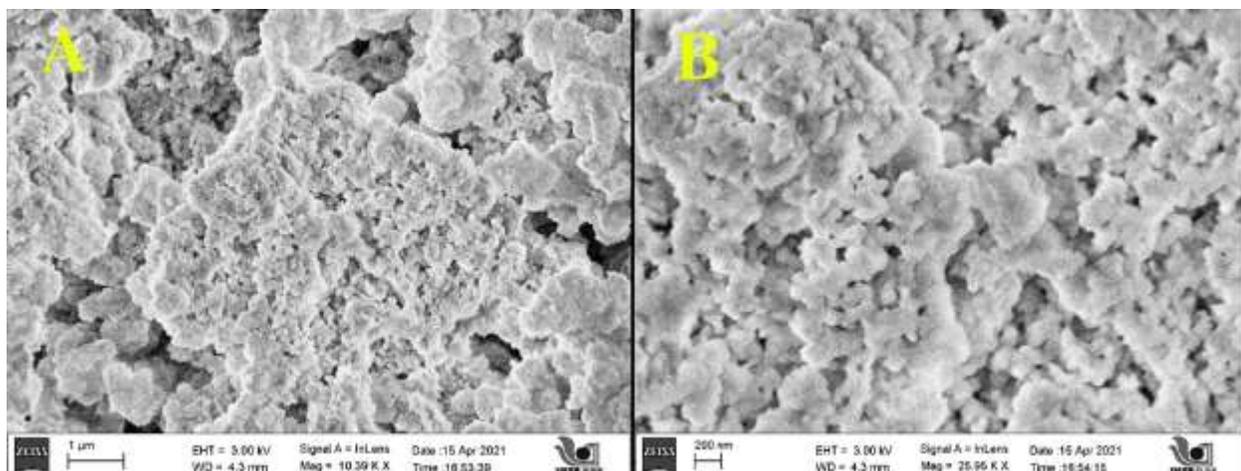


Figure S9. A & B: Field Emission Scanning Electron Microscopy (FESEM) images of the COF. From the FESEM images, the fluffy cotton-like morphology of the COF can be observed.

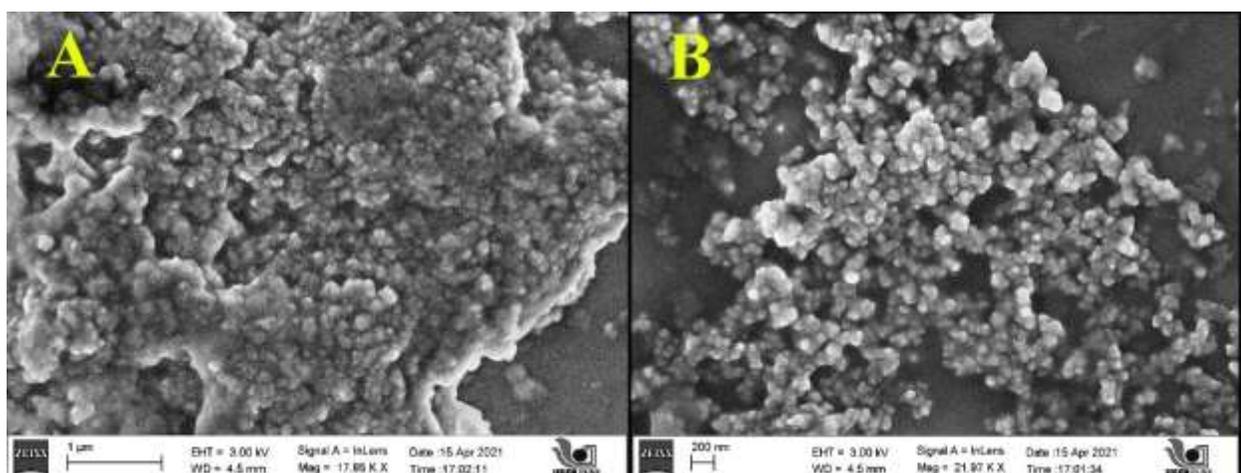


Figure S10. A & B: Field Emission Scanning Electron Microscopy (FESEM) images of the CoCOF.

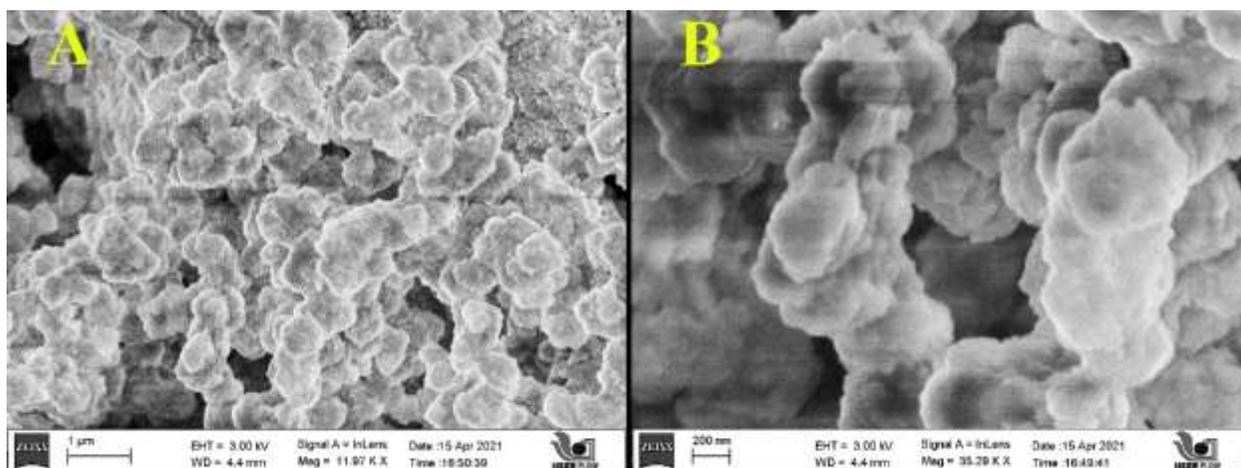


Figure S11. A & B: Field Emission Scanning Electron Microscopy (FESEM) images of the AuCOF.

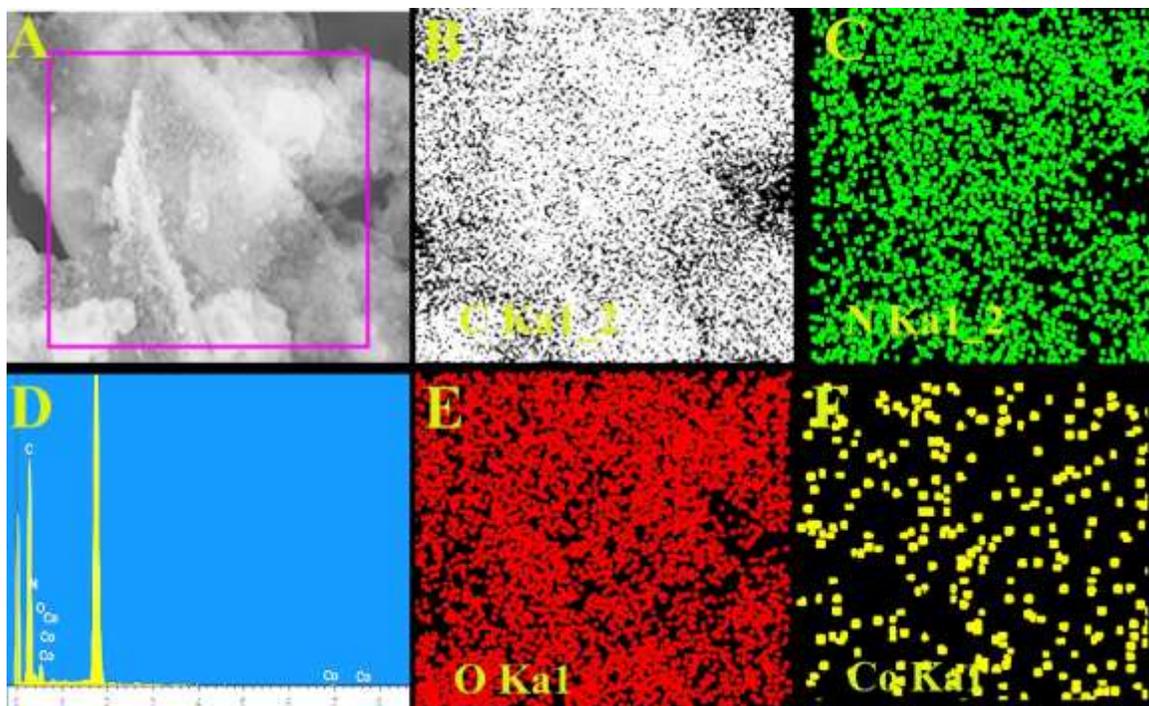


Figure S12. The energy dispersive X-ray analysis (EDAX) assisted elemental mapping reveals the homogeneous distribution of Co in CoCOF.

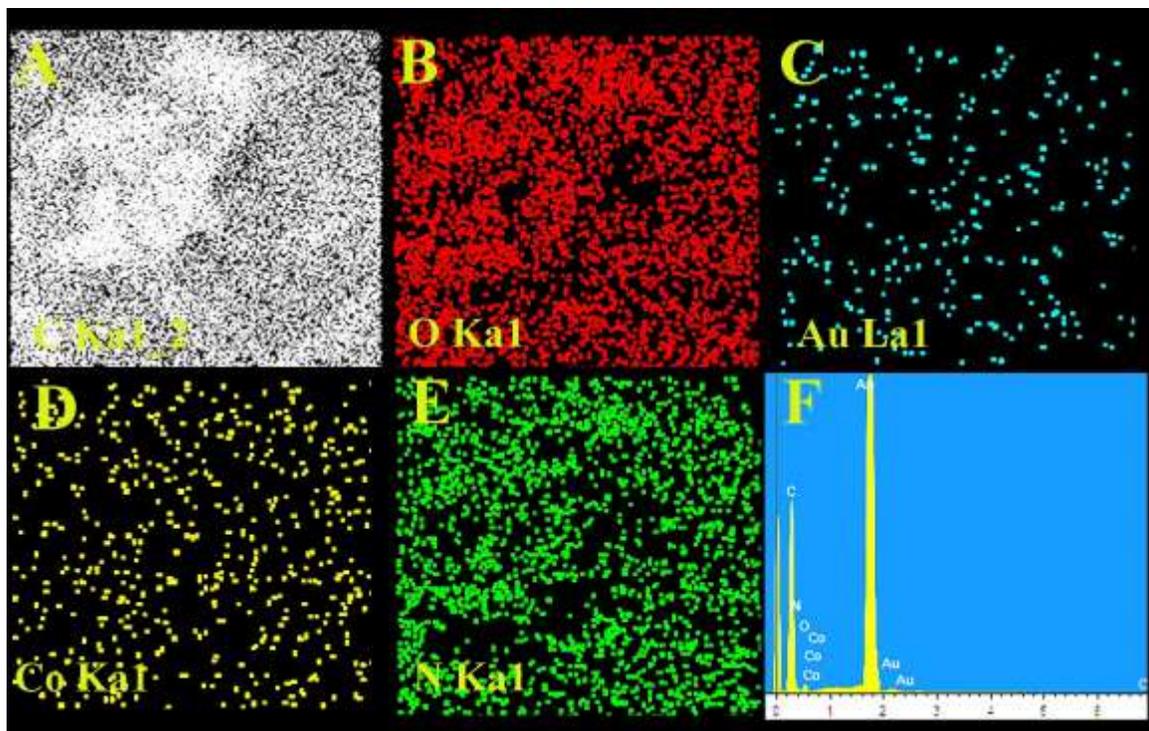


Figure S13. The energy dispersive X-ray analysis (EDAX) assisted elemental mapping reveals the homogeneous distribution of Co and Au in AuCoCOF.

Elements	Weight %	Atomic %
C K	58.35	64.27
N K	20.90	19.74
O K	18.82	15.56
Co K	1.93	0.43
Total	100	

Figure S14. EDX data of the CoCOF.

Note: Similar type of fractional values are reported in Wang et al J. Am. Chem. Soc. 2018, 140, 39, 12345– 12348. Shirsath et al J Nanopart Res 2013, 15, 1976.

Elements	Weight %	Atomic %
C K	70.99	77.14
N K	15.94	14.86
O K	9.47	7.73
Co K	0.24	0.05
Au K	3.35	0.22
Total	100	

Figure S15. EDX data of the AuCoCOF.

Note: Similar type of fractional values are reported in Wang et al J. Am. Chem. Soc. 2018, 140, 39, 12345– 12348. Shirsath et al J Nanopart Res 2013, 15, 1976.

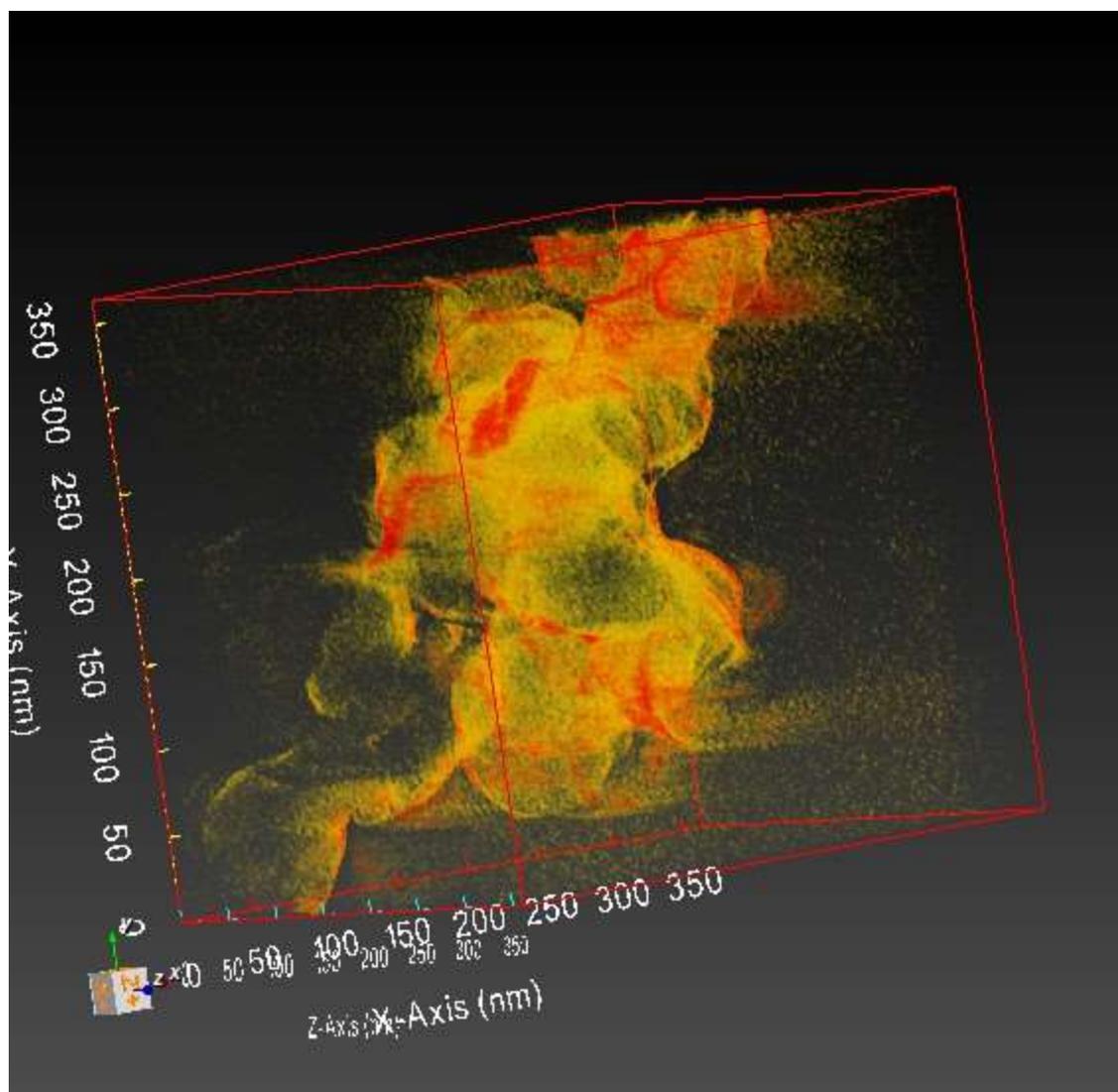


Figure S16. Tomographic images along the axis show the cotton-like morphology of AuCoCOF along with the homogenous distribution of particles of Au and Co species. The red region indicates nanoparticles while the yellow region corresponds to the COF.

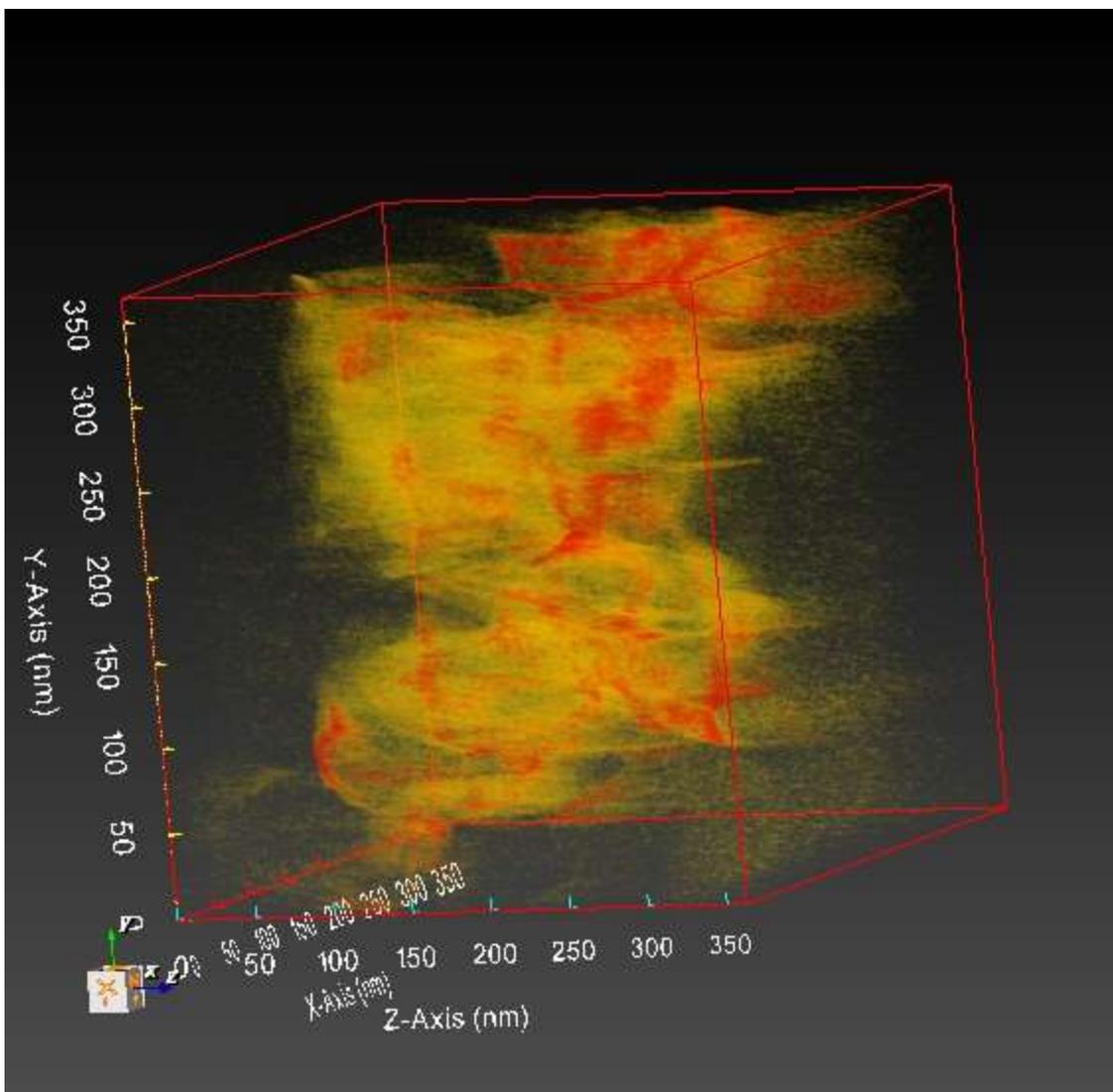


Figure S17. Tomographic images along the axis shows the cotton-like morphology of AuCoCOF along with the homogenous distribution of particles of Au and Co species. The red region indicates nanoparticles while the yellow region corresponds to the COF.

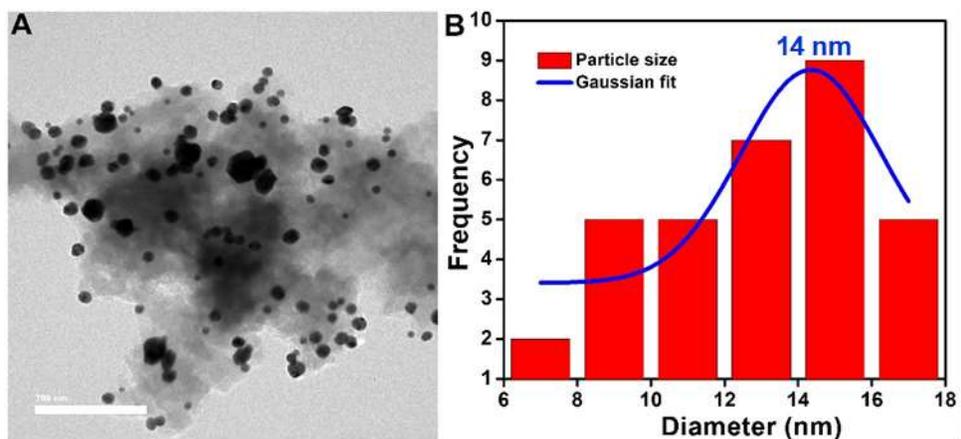


Figure S18. HRTEM image and corresponding particle size distribution from HRTEM; the average particle size is 14 nm.

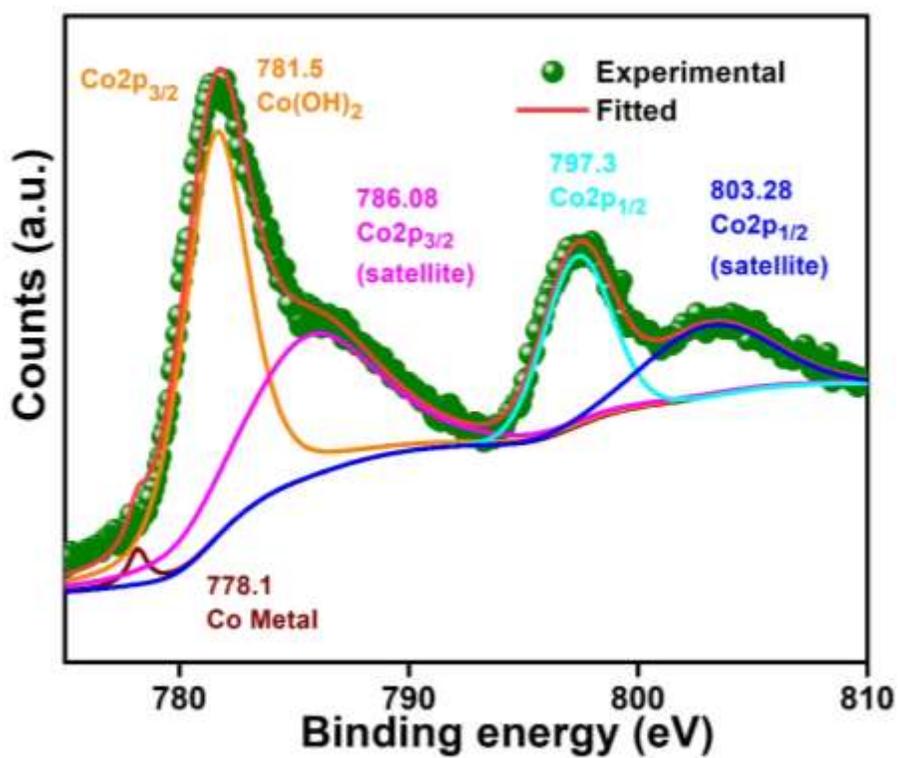


Figure S19. Co₂p XPS spectra of CoCOF.

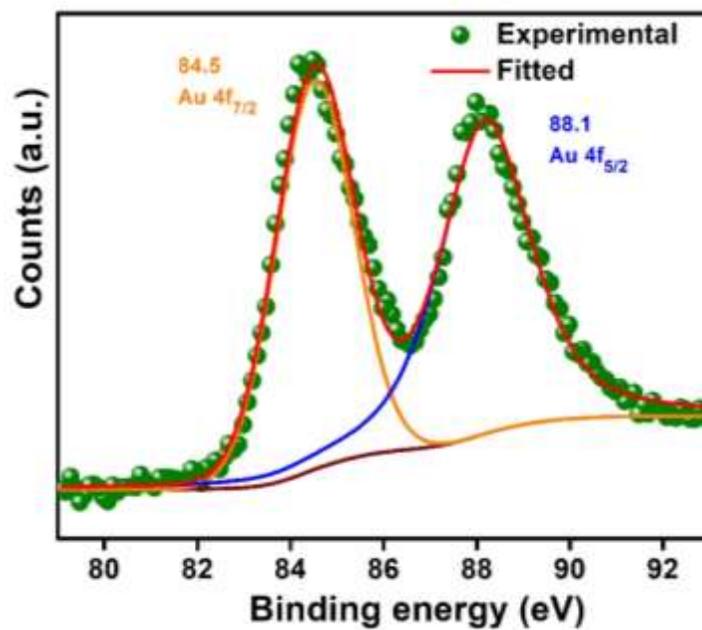


Figure S20. Au4f XPS spectra of AuCoCOF sample.

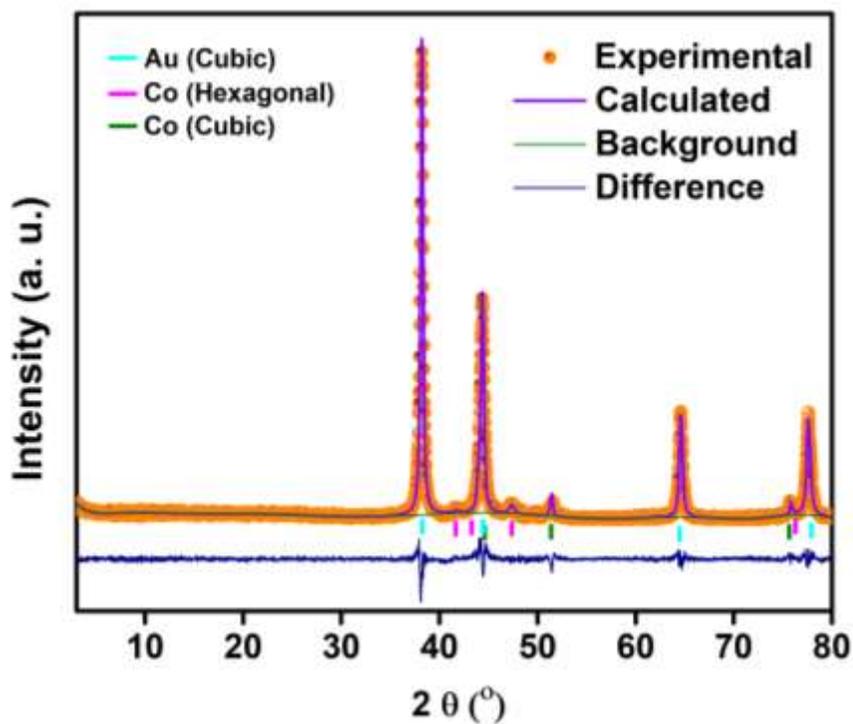


Figure S21. A fit from the Reitveld refinement of the calcined sample of AuCoCOF. The peaks due to the Au (metal) can be seen (cyan) and matched well with the standard Au (JCPDS: 04-0784); Co(Hexagonal: JCPDS: 05-0727) (pink) and Co (Cubic; ICSD: 44989) (green).

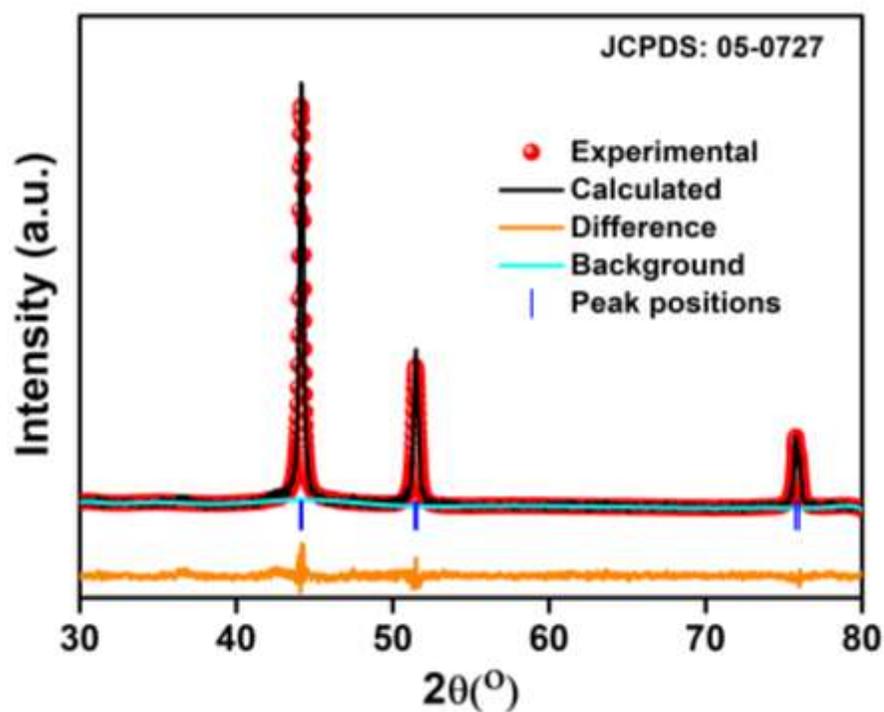


Figure S22. A fit from the Reitveld refinement of the calcined sample of CoCOF. The peaks due to the Co (metal) can be seen and matched well with the standard metallic cobalt (JCPDS: 05-0727).

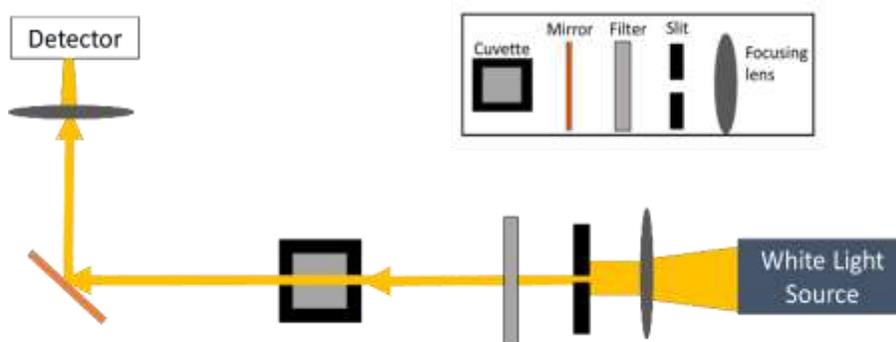


Figure S23. Schematic of the optical setup used to monitor dye reduction.

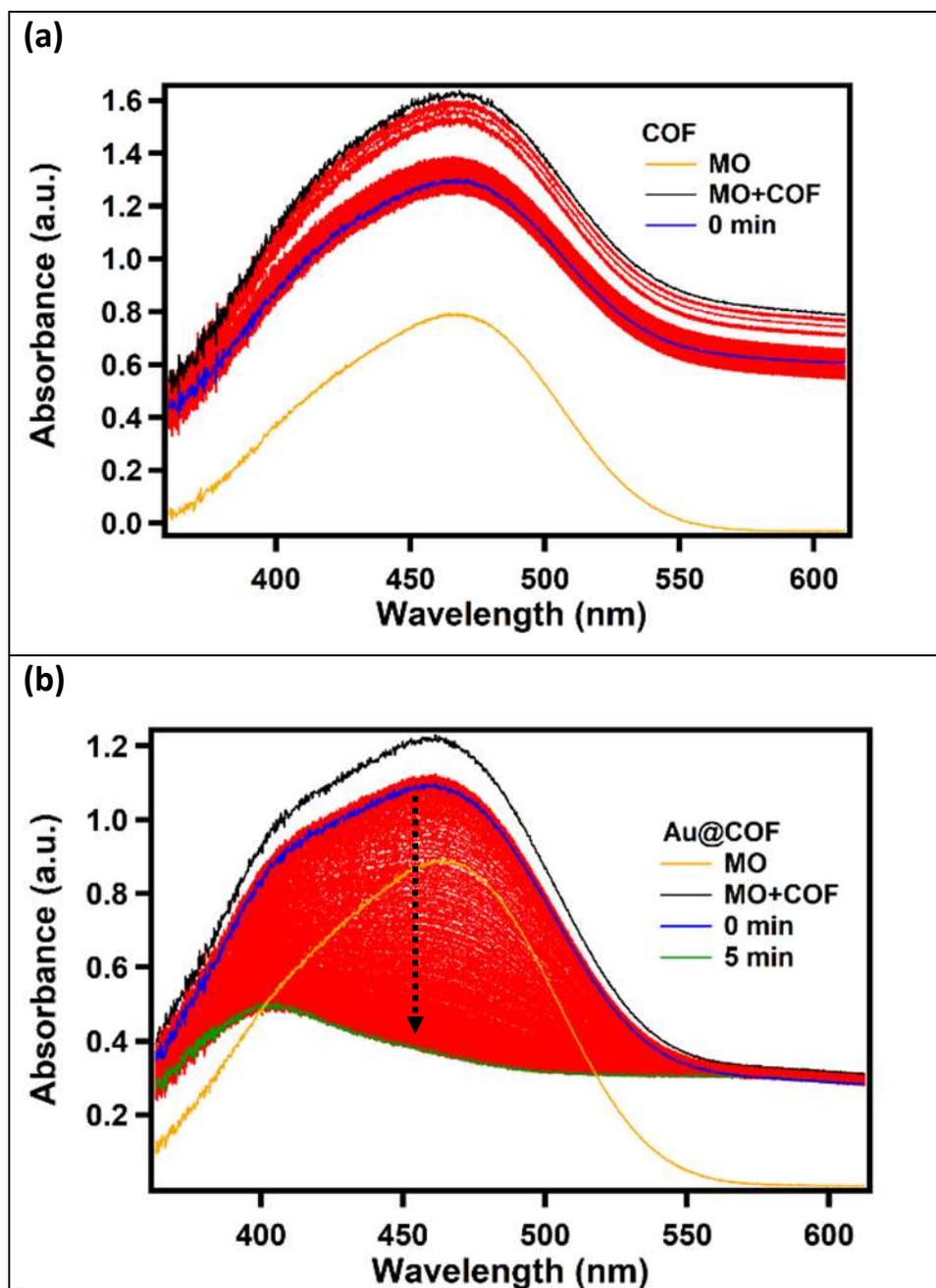


Figure S24. Time dependent, in-situ UV-vis spectra of methyl orange (MO) reduction by a) Pristine COF b) AuCOF acquired every 1 sec for 5 minutes. The offset in absorbance is due to scattering by catalyst particles.

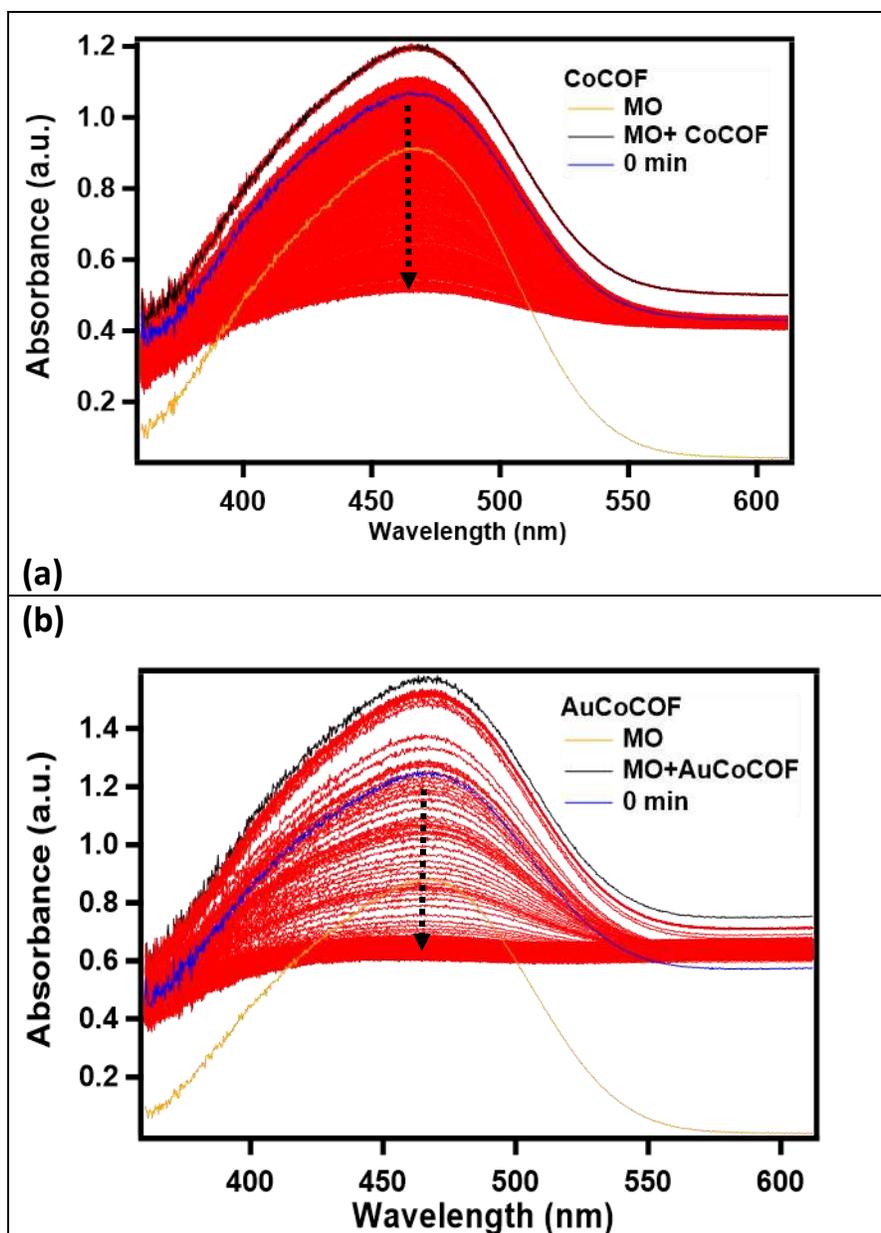


Figure S25. Time-dependent, in-situ UV-vis spectra of methyl orange (MO) reduction by a) CoCoF acquired every 1 sec for 10 mins b) AuCoCoF acquired every 1 sec for 5 mins. The offset in absorbance is due to scattering by catalyst particles.

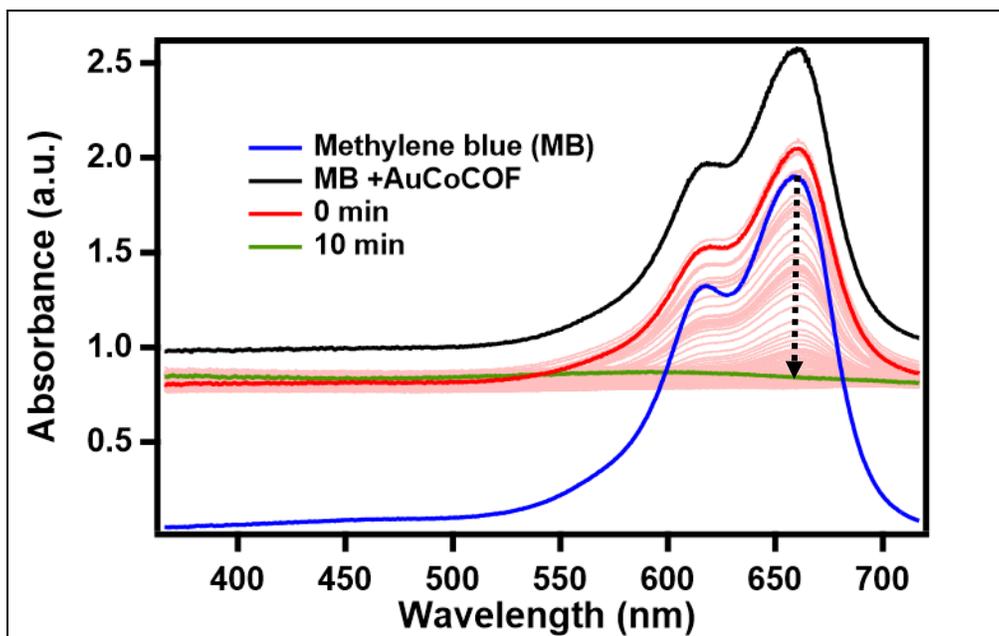


Figure S26. Time dependent UV-Vis spectra of methylene blue reduction by AuCoCOF acquired every 1 sec for 10 mins. The offset in absorbance is due to scattering by catalyst particles

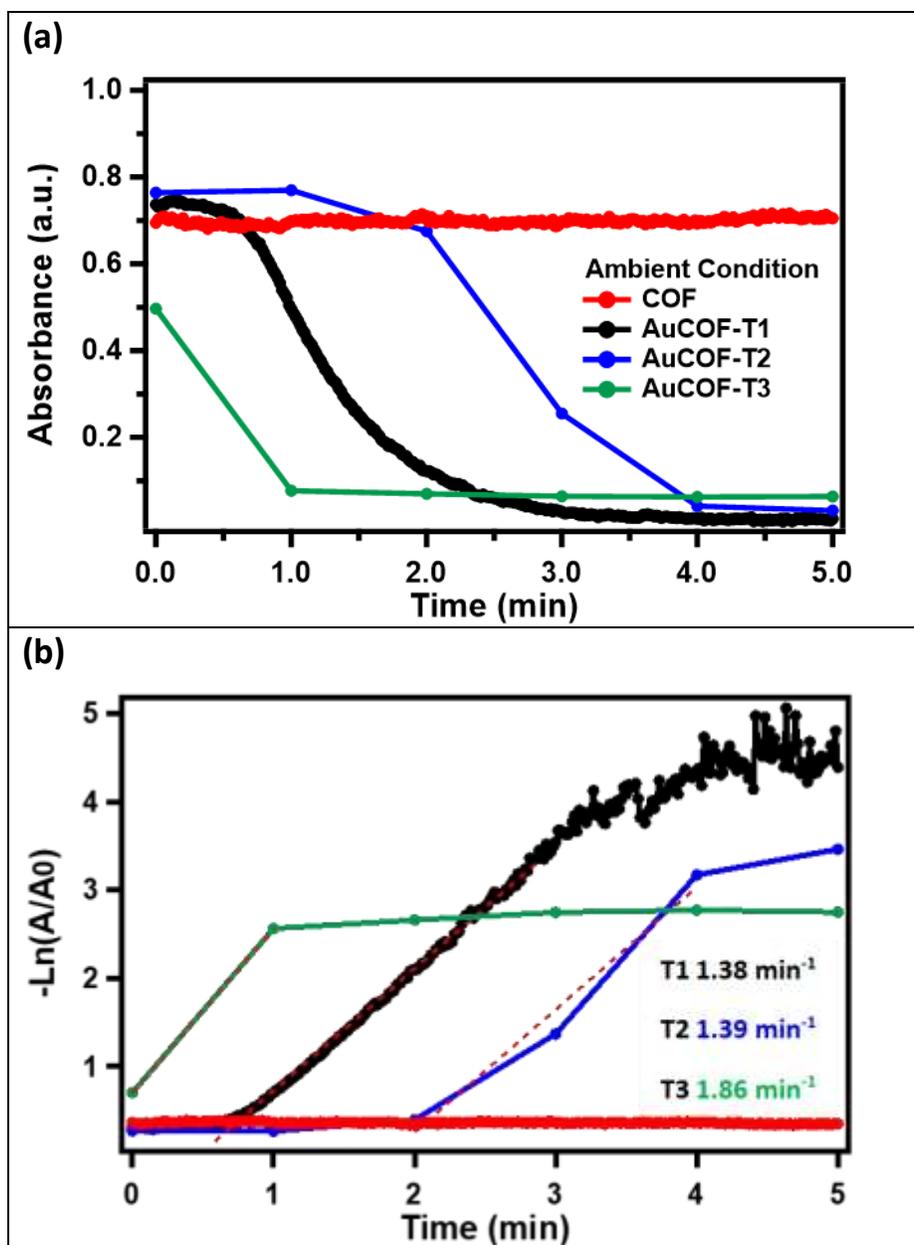


Figure S27. Repeat experiments performed using different batches of AuCOF, plotted using Figure S24. A) Intensity at 464 nm vs. time plot tracking methyl orange reduction and b) associated Ln (absorbance) plots fitted with pseudo first-order kinetics to obtain values of rate constants. T1, T2, T3 indicate different trials of methyl orange reduction.

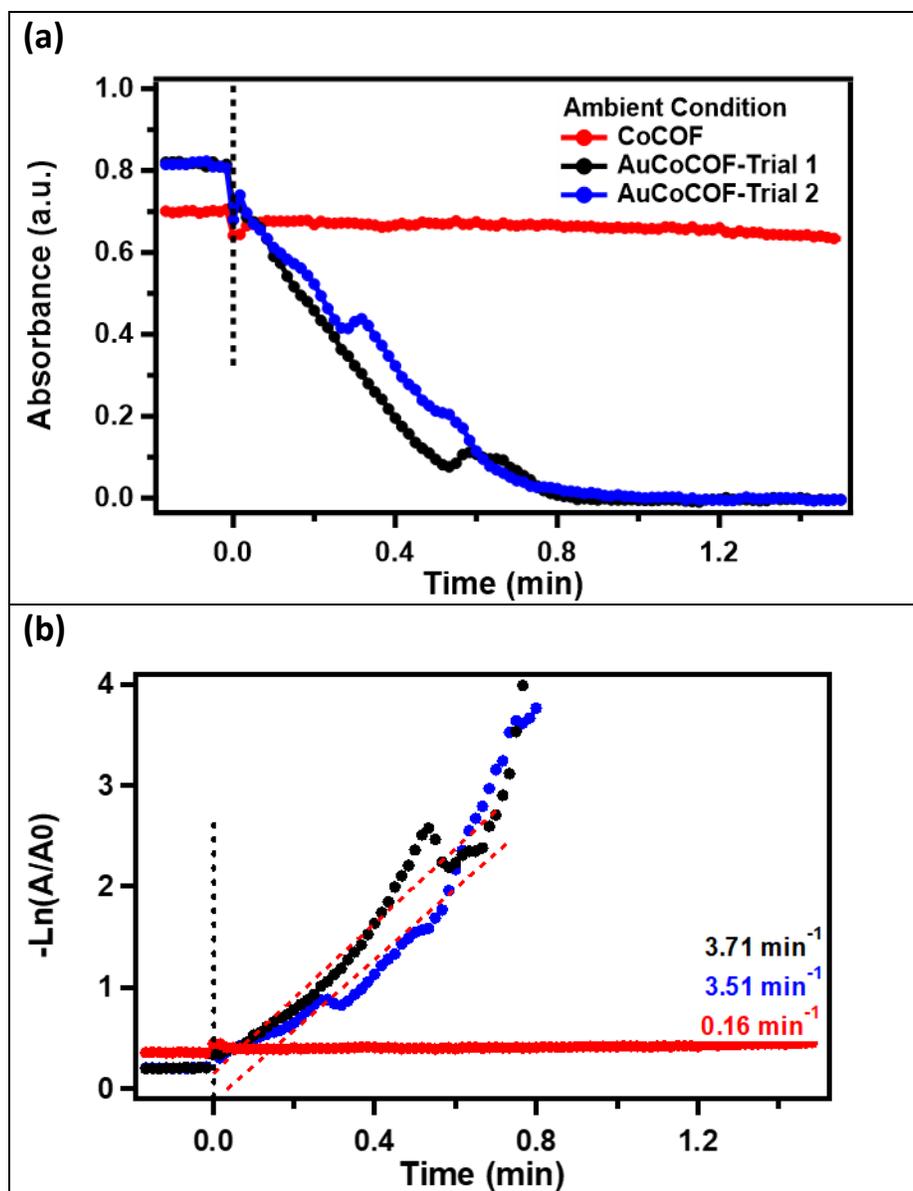


Figure S28. Repeat experiments performed using different batches of AuCoCOF, plotted using Figure S25. A) Intensity at 464 nm vs. time plot tracking methyl orange reduction and associated b) Ln plots fitted with pseudo first-order kinetics to obtain values of rate constants.

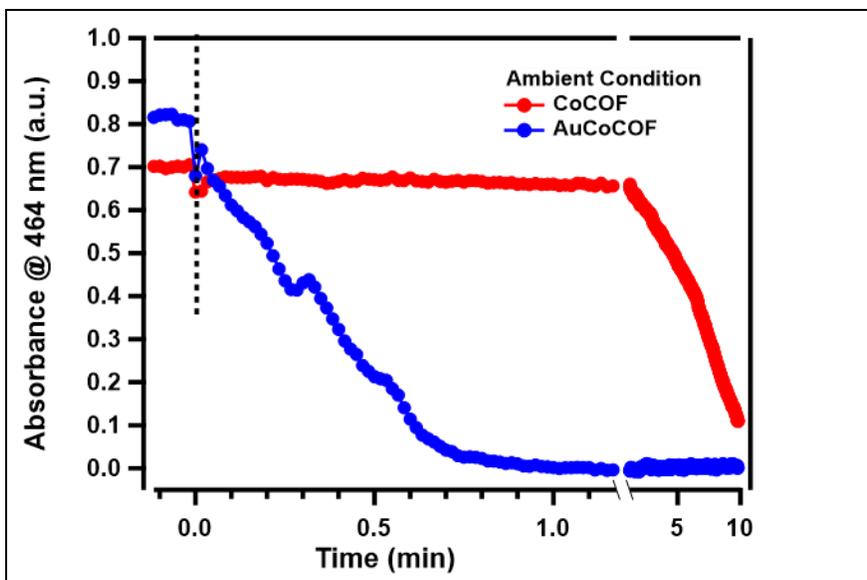
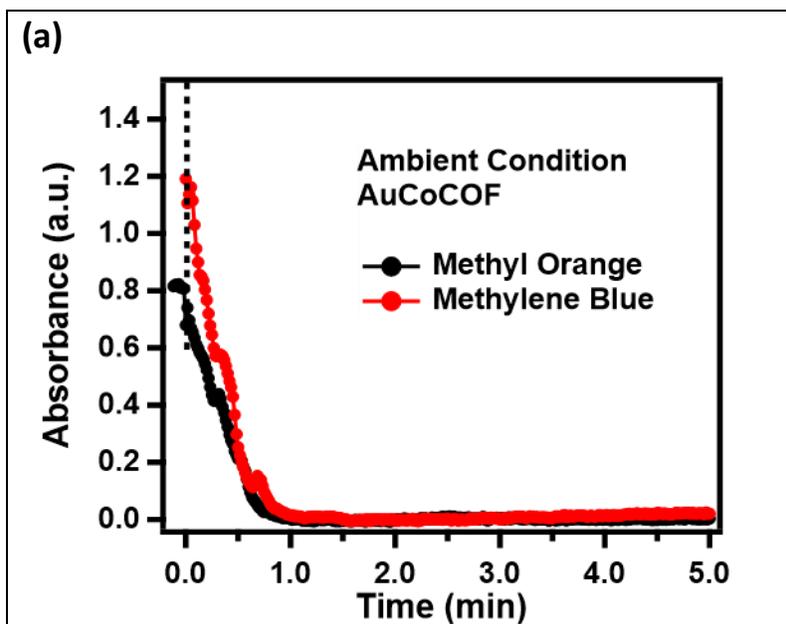


Figure S29. Absorbance (at 464 nm) vs time, plotted using Figure S25, showing methyl orange reduction using CoCOF hybrids for 10 minutes



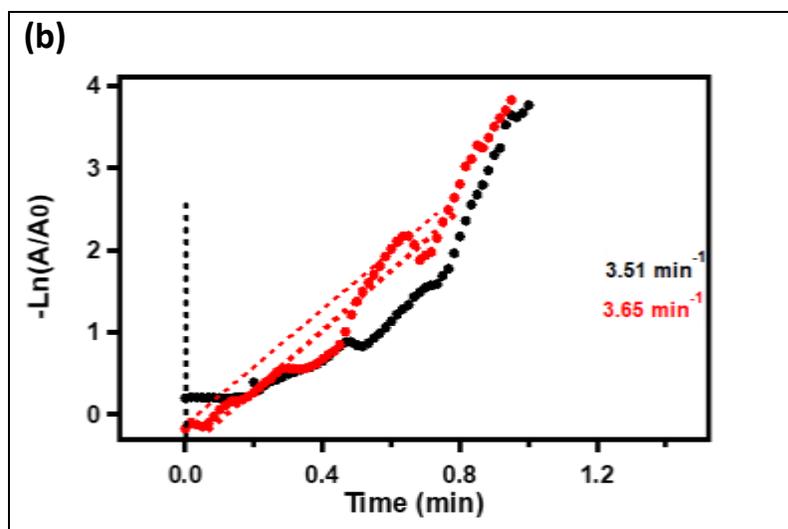


Figure S30. The plot of absorbance vs. time tracking reduction of methyl orange (black) in comparison with methylene blue (red) using AuCoCOF plotted using Figure S25, S26. B) Corresponding Ln plots fitted with pseudo first-order kinetics to obtain values of rate constant.

Test to check for leaching of nanoparticles during dye reduction

In order to evaluate the stability of the AuCoCOF and find out if the nanoparticles were leaching into the solution during catalysis, AuCoCOF was dispersed in water and stirred for 15 mins. Then the COF is filtered out and the filtrate was used to study methyl orange reduction. No appreciable reduction of methyl orange was observed (Figure S31) using the filtrate, revealing the high stability of the nanoparticles in the AuCoCOF.

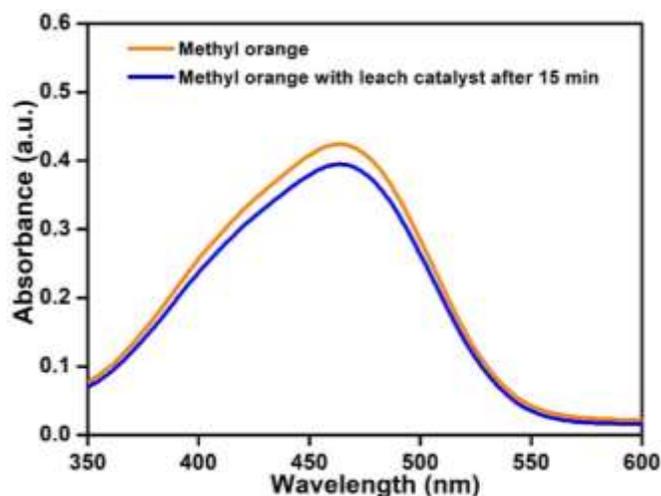


Figure S31. In-situ UV-vis spectra of methyl orange reduction using the supernatant from the AuCoCOF dispersion as the catalyst.

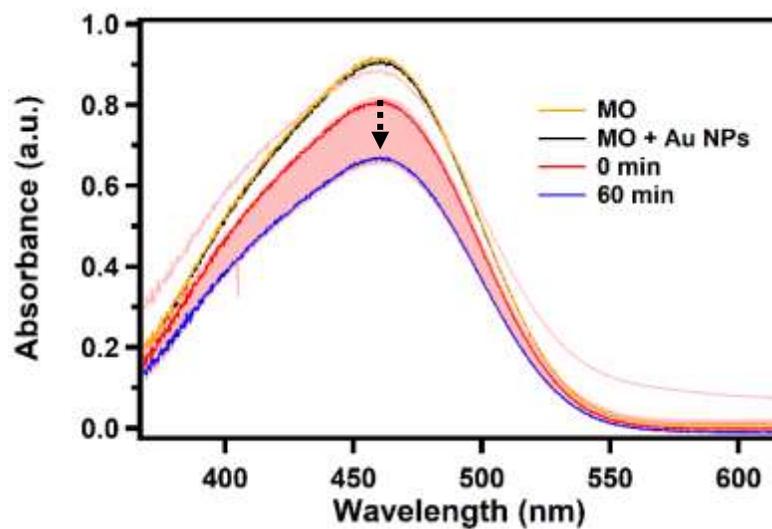


Figure S32. Time-dependent UV-Vis spectra of methyl orange reduction using Au NPs acquired every 1 min for one hour.

In situ Spectroelectrochemistry:

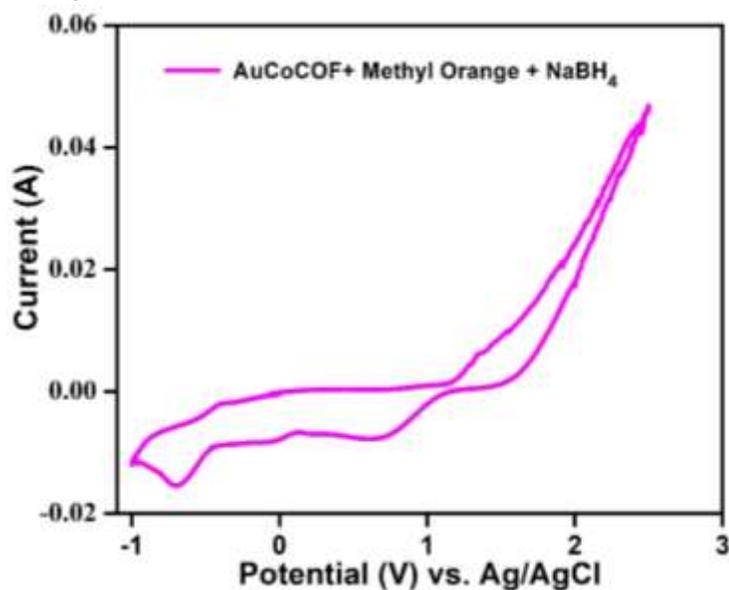


Figure S33. Three-electrode CV data was recorded during spectroelectrochemistry measurement of methyl orange reduction at 100 mV/s scan rate using Pt mesh as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode.

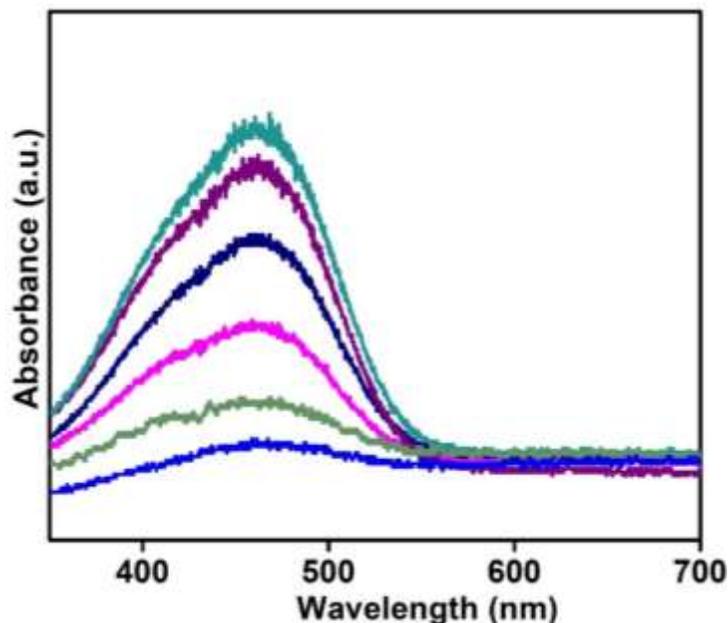


Figure S34. Time dependent in-situ UV-Vis spectroscopy of methyl orange reduction data was recorded under applied potential (0.7 V) in three electrode setup using Pt mesh as working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode.

Table S1. Catalytic rate of various catalysts for methyl orange reduction compared to this study.

Catalyst	Amount of Catalyst	Amount of Methyl Orange	Rate:
MIL-100 (Fe) ^[S3]	0.25 g	5 ppm 750 mL	7 hr: 40% Degraded in sunlight 64% under UV
UTSA-38 ^[S4]	0.2 g	50 ml of 20 mg/L	100% Degradation in 120 minutes under UV
Ag@TPHH-COF ^[S5]	0.5 g	10 ml, 2.5*10 ⁻⁴ M	0.0180s ⁻¹ =1.08 min ⁻¹ Use 0.5 g NaBH ₄
AuCoCOF (Present Study)	0.25 mg	2 ml, 40 mM	3.60±0.16 min⁻¹ 250 µl NaBH₄ (100 mM)

References:

S1. Mullangi, D.; Nandi, S.; Shalini, S.; Sreedhala, S.; Vinod, C. P.; Vaidhyanathan, R. Pd loaded amphiphilic COF as catalyst for multi-fold Heck reactions, CC couplings and CO oxidation. *Sci. Rep.* **2015**, *5*, 1-12.

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- S3.** Guesh, K.; Caiuby, C. A. D.; Mayoral, A.; Diaz-Garcia, M.; Diaz, I.; Sanchez-Sanchez, M. Sustainable Preparation of MIL-100(Fe) and Its Photocatalytic Behavior in the Degradation of Methyl Orange in Water. *Cryst. Growth Des.* **2017**, *17*, 1806-1813.
- S4.** Das, M. C.; Xu, H.; Wang, Z.; Srinivas, G.; Zhou, W.; Yue, Y.; Nesterov, V. N.; Qian, G.; Chen, B. A Zn₄O-containing doubly interpenetrated porous metal-organic framework for photocatalytic decomposition of methyl orange. *Chem. Commun.* **2011**, *47*, 11715-11717.
- S5.** Wang, R.; Li, D.; Wang, L.; Zhang, X.; Zhou, Z.; Mu, J.; Su, Z. The preparation of new covalent organic framework embedded with silver nanoparticles and its applications in degradation of organic pollutants from waste water. *Dalton Trans.* **2019**, *48*, 1051-1059.