Supporting Information

# Pd Nanoparticles Decorated Covalent Organic Frameworks for Enhanced Photocatalytic Tetracycline Hydrochloride Degradation and Hydrogen Evolution

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## Experimental methods

*Synthesis of COF*: A 10 ml pyrex tube was charged with 1,3,5-benzenetricarboxaldehyde (7.8 mg) and 5,5'-dicynide-2,2'-bipyridine (16.9 mg) o-Dichlorobenzene (0.5 mL), n-butanol (1.5 mL) and aqueous $Cs_2CO_3$ (23.5 mg), and then the suspension was sonicated for 5 min, degassed with three freeze-pump-thaw cycles (liquid nitrogen bath), sealed under vacuum and heated at 120 °C for three days. After cooling down, the solid was collected by centrifugation, washed twice with dichloromethane, methanol and tetrahydrofuran successively. The resulting power was packed in the tightly in the Soxhlet extractor and methanol (250 ml) was used as a solvent for extraction. The process was carried out for 24 h. The obtained powder was dried at 80 °C under vacuum overnight.

*Synthesis of Metal-COFs:* A methanol suspension containing COF (100 mg) and $CoCl_2$ (or $H_2PdCl_4$ or $H_2AuCl_4$, 0.2 mmol) was refluxed overnight under nitrogen protection, and the cooled precipitate was collected by filtration, washed with water and methanol, followed by drying at 80 °C under vacuum overnight. The contents of Co, Au and Pd were determined to be 2.34 %, 3.45 % and 2.56 % by Inductively coupled plasma-mass spectrometry (ICP-MS), respectively.

*Material characterizations:*

The crystal phases of the photocatalysts were determined by a powder X-ray diffractometer (XRD, Rigaku Ultima III, Japan) operated at 20 kV and 40 mA with Cu-Ka radiation. The surface morphology was examined using scanning electron microscopy (SEM, FEI Nova Nano SEM 230, USA). Elemental compositions were measured by energy dispersive X-ray spectroscopy (EDX) (Oxford Instruments) at 200 kV and calibrated with standard Cu and Co target before testing. Scanning transmission electron microscopy (STEM, Tecnai TF-30, operated at 300 kV) were

conducted for elemental mapping. Diffused reflectance spectrum was scanned using a UV-vis spectrophotometer (UV-2500, Shimadzu Co., Japan) and transformed into absorption spectrum according to the Kubelka–Munk relationship. ICP-MS analysis was conducted to analyze the composition in catalysts using an Agilent 7700 instrument.

**Photocatalytic and photoelectrochemical measurements**: The electrochemical measurements were carried out with a three-electrode system controlled by a Gamry electrochemical workstation at room temperature. As for the three-electrode system, the as-prepared samples were served directly as the working electrode clamped by a platinum electrode holder with a platinum sheet electrode and an Ag/AgCl as the counter electrode and reference electrode, respectively. Photoelectrochemical performance was measured in 0.5 M $Na_2SO_4$ solution electrolyte. A 300 W xenon lamp was used as the light source, and the potentials were displayed versus reversible hydrogen electrode (RHE) by: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.197 + 0.0591 \times pH$. Transient photocurrent measurement was conduct at open circuit potential with a voltage amplitude of 10 mV using the same three-electrode system. The Mott- Schottky relationship can be expressed by: $C_{sc}^{-2} = 2(E-E_{fb}-kT/e)/e\varepsilon\varepsilon_0NA^2$, where $C_{sc}$ is the capacitance of the space charge region, and $\varepsilon$ is the dielectric constant of the semiconductor (assumed value of 80 for these calculations), and $\varepsilon_0$ is the permittivity of free space, and $k$ is the Boltzmann constant, and $T$ is the temperature, and $e$ is the charge of an electron, and $A$ is the electrode surface areas, and $N$ is the donor density. Majority charge carrier concentration could, thus, be estimated from the slope of Mott-Schottky plot.

A photocatalytic reactor with a quartz window was used, and a 300-W Xe lamp (full spectrum) was adopted as the light source. A photocatalyst (0.5 g L$^{-1}$) was added to a reactor with water as the solvent. The concentration of tetracycline hydrochloride (Tet) is 10 mg L$^{-1}$. The solution was kept in dark for at least 30 min for equilibrium before illumination. The photocatalytic degradation rate was measured by UV-Vis. After 80 min measurement, the photocatalysts were filtered and washed with deionized water. This measurement was repeated for 8 times.

For the radical scavenging measurement, different radical scavengers such as p-benzoquinone, triethanolamine and ethanol with a concentration of 10 mmol L$^{-1}$ were used. The impact of scavengers' presence on Tet degradation was analyzed by measuring the change of Tet concentration after a certain time period.

*Radical scavenging and photocatalytic hydrogen evolution tests*

In a typical test, 1 mmol scavenger, such as p-benzoquinone, triethanolamine and ethanol was added into the Pd-COF photodegradation system, respectively, to suppress the TC photodegradation. The photocatalytic hydrogen evolution experiment was conducted under vacuum in a 500 mL quartz reactor with a top quartz window to allow light irradiation (CEL-SPH2N, CEAULIGHT Beijing). Typically, 30 mg photocatalyst was added into a 210 mL triethanolamine solution (10 vol%) which was used as a hole sacrificial agent and kept under ultrasonic treatment for 15 min. A 300 W Xe lamp equipped with a 420 nm cut-off filter (UVCUT420, PerfectLight, China) was used as an artificial sunlight source. Prior to light irradiation, the quartz reactor was sealed to a gas-tight condition with high vacuum grease and purged by using a vacuum pump to remove residual air. During the hydrogen generation reaction, the suspension was exposed to simulated solar light irradiation under continuous stirring. The volume of generated hydrogen was analyzed by using an on-line gas chromatograph with a thermal conductivity detector (TCD) at set intervals.

**Computational details:** The density functional theory (DFT) calculations were made with the Vienna Ab Initio Simulation Package code. The exchange correlation interactions and the ion–

electron interactions were solved by the Perdew–Burke–Ernzerhof and Heyd-Scuseria-Ernzerhof exchange-correlation functionals.[1] For primitive unit cell, a G-centered 4x4x1 $k$-mesh were used and for 3×3×1 supercell, a G-centered 4x4x1 $k$-mesh were used to simulated the doped structure. A plane-wave cutoff of 450 eV was adopted and the maximal force on all-atom was below 0.01 eV/Å. The distance between periodic units in the vertical direction was larger than 16 Å.[2] The DFT-D2 method of Grimme was used in all calculations to accurately describe long-range Van der Waals (vdW) interactions. The localized Co 3$d$, Au and Pd 4$d$ electronic interactions were treated with DFT + U method with $U_{eff}$ = 3.32 eV, 3.50 eV and 5.00 eV, respectively.[3]
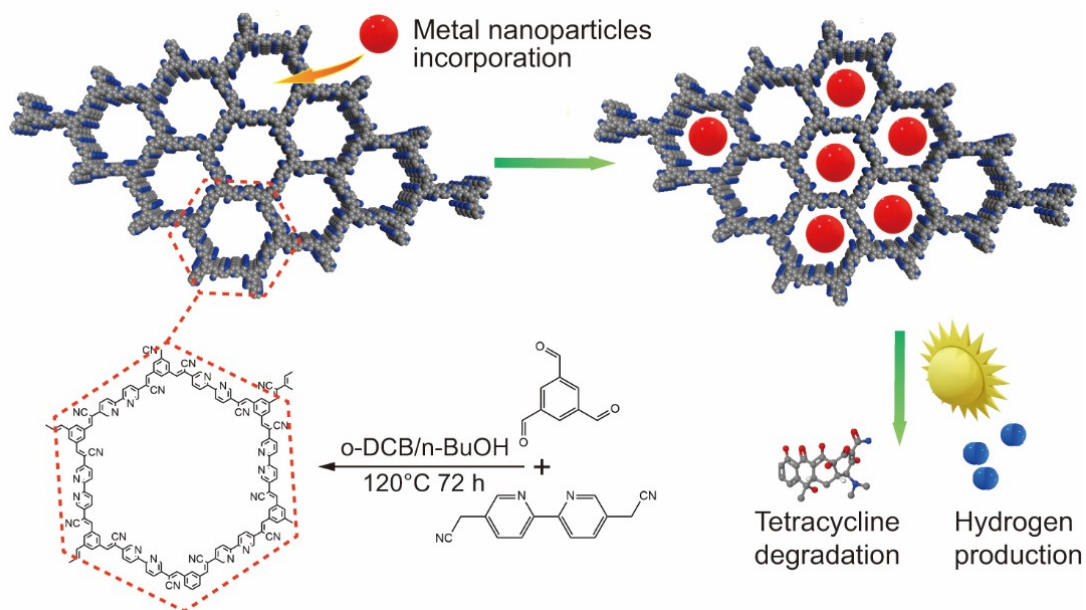
**Scheme 1.** Schematic illustration of synthesizing sp$^2$-carbon-linked COFs and metal-decorated COFs for photocatalytic hydrogen evolution and tetracycline hydrochloride degradation. Gray balls: carbon, blue balls: nitrogen and red balls: metal nanoparticles.
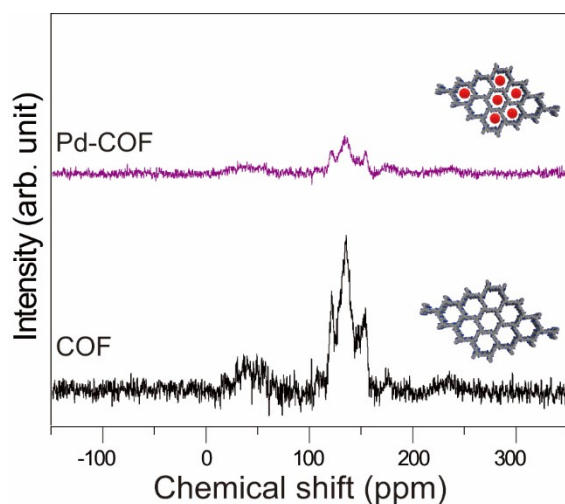


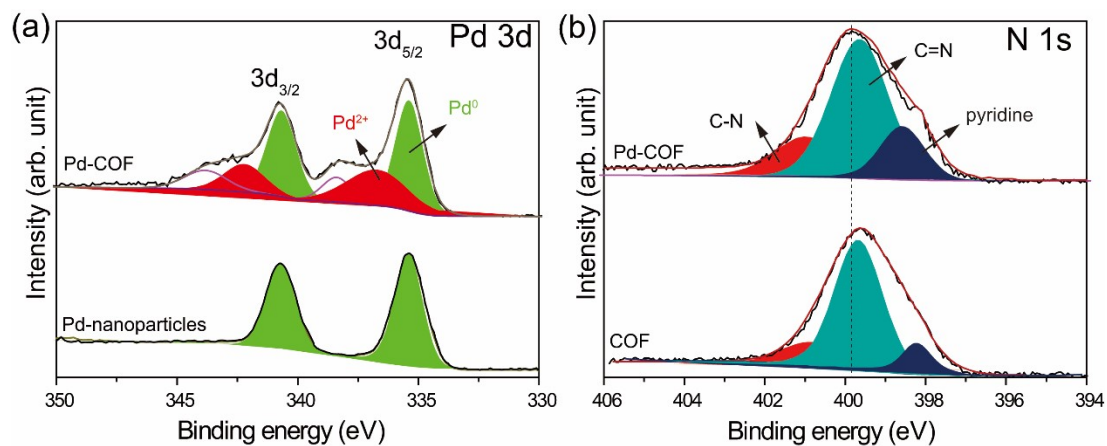**Fig. S1**. Solid-state $^{13}$C CP/MAS NMR spectra of COFs and Pd-COFs.



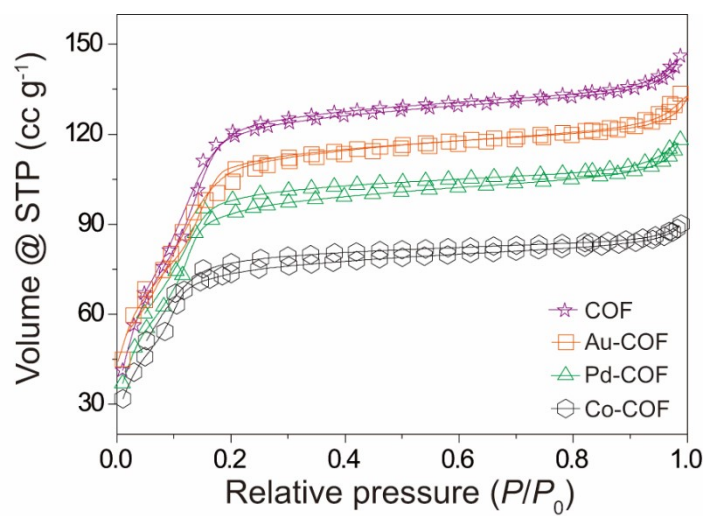**Fig. S2**. Pd 3d (a) and N1s (b) X-ray photoelectron spectroscopy spectra of COF, Pd and Pd-COFs.

**Fig. S3**. N$_2$ adsorption-desorption isotherms of COFs, Co-COFs, Au-COFs and Pd-COFs, respectively.
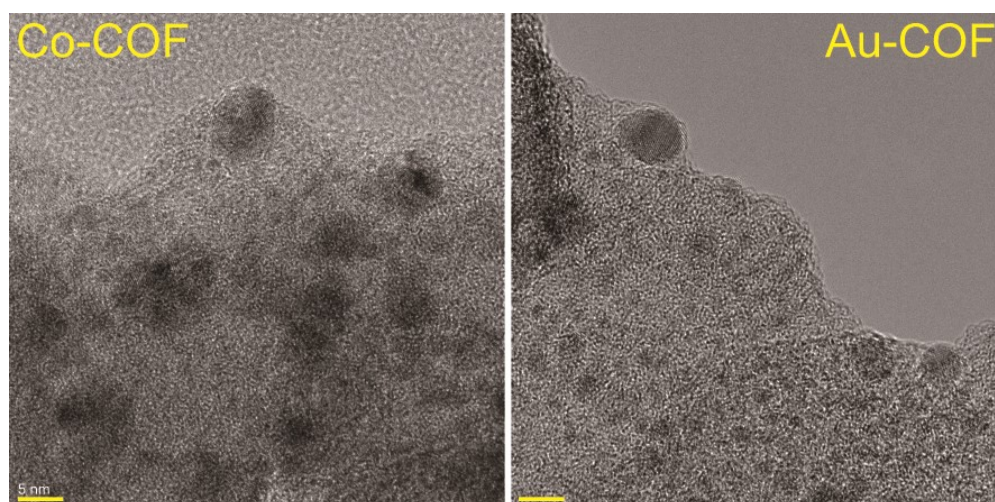


**Fig. S4.** HRTEM images of Co-COFs and Au-COFs.
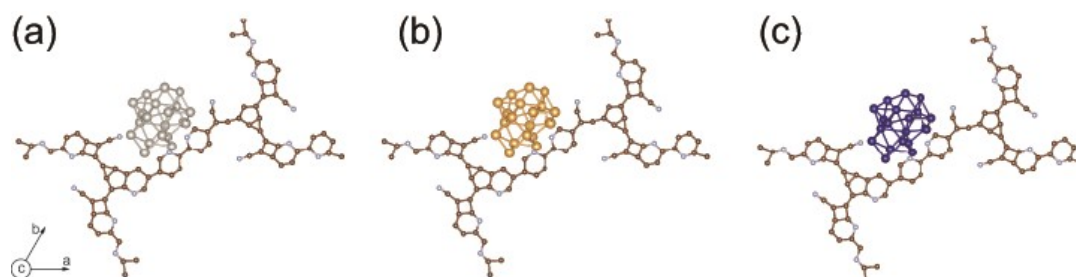


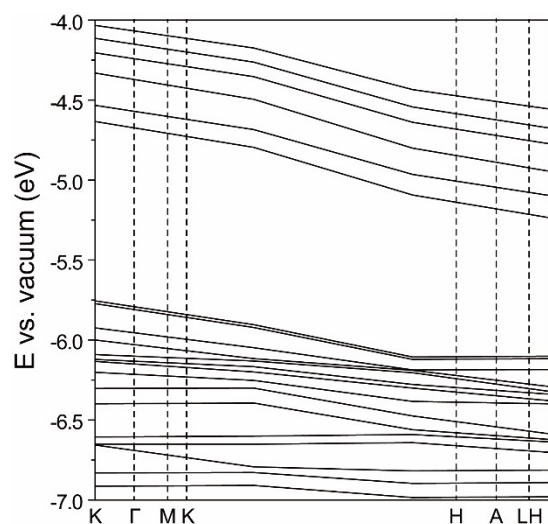**Fig. S5.** Structural models of COFs, Co-COFs, Au-COFs and Pd-COFs used for DFT calculations.

**Fig. S6.** Calculated band structure of the COF.

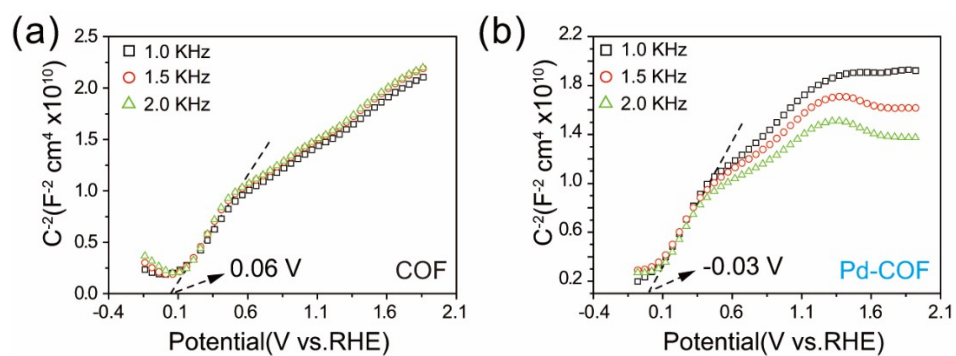The Band structure analysis shows an indirect band gap structure for the COF.



**Fig. S7.** Mott−Schottky plots of COFs (a) and Pd-COFs (b) in $Na_2SO_4$ solution (pH = 7).
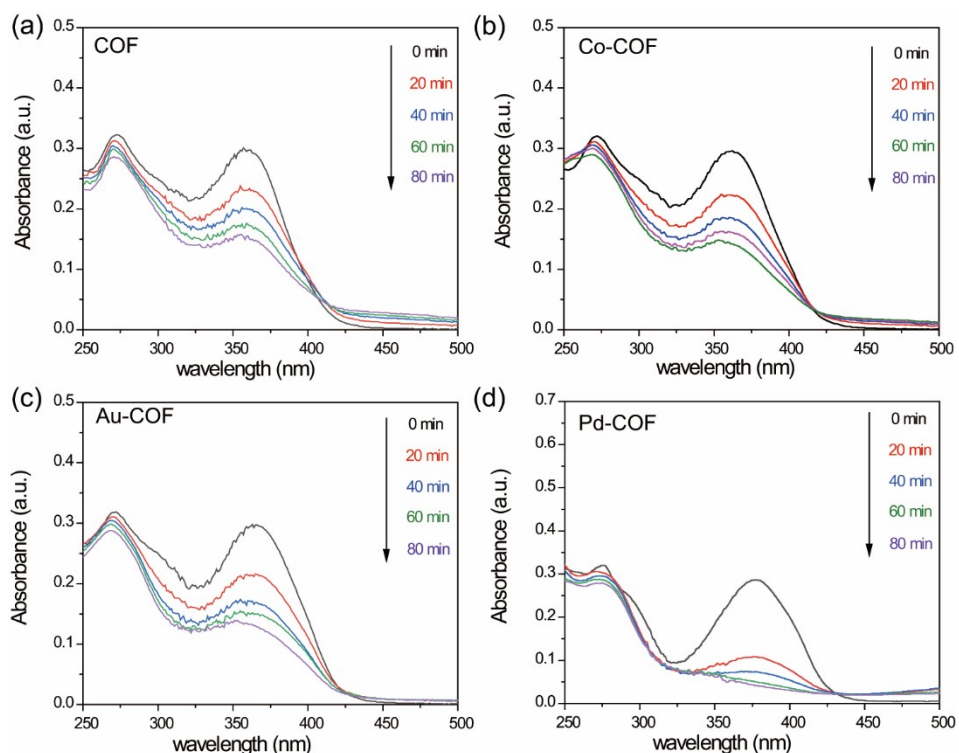
**Fig. S8.** Time-dependent UV-vis absorption spectra of tetracycline hydrochloride in the presence of COFs (a), Au-COFs (b), Co-COFs (c) and Pd-COFs (d), respectively under irradiation.
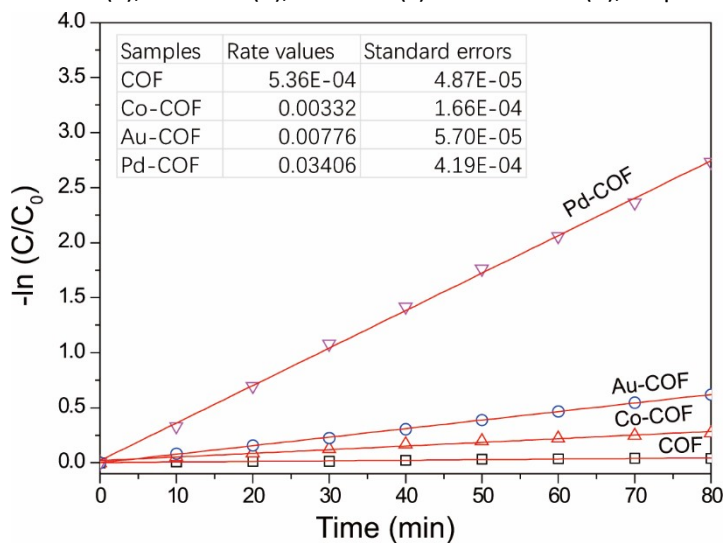


| Samples | Rate values | Standard errors |
|---------|-------------|-----------------|
| COF     | 5.36E-04    | 4.87E-05        |
| Co-COF  | 0.00332     | 1.66E-04        |
| Au-COF  | 0.00776     | 5.70E-05        |
| Pd-COF  | 0.03406     | 4.19E-04        |

**Fig. S9.** Linear fitting and corresponding rate constants (inserted table) for photocatalytic Tet degradation of COFs, Co-COFs, Au-COFs and Pd-COFs.
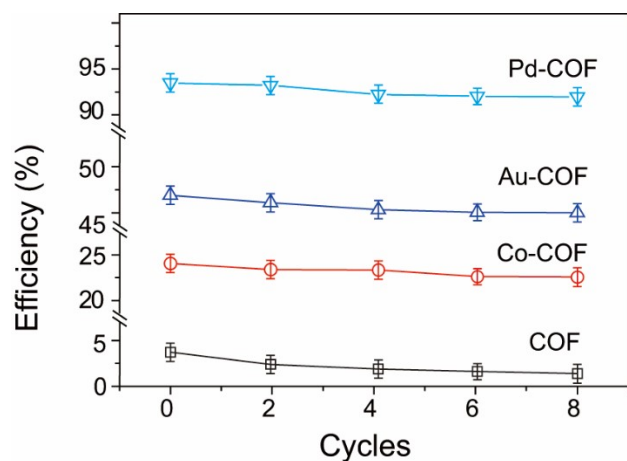
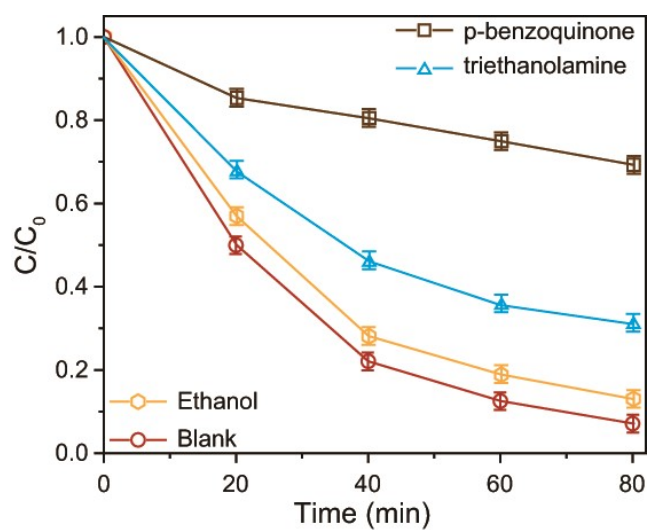**Fig. S10.** Cycling stability of COFs, Co-COFs, Au-COFs and Pd-COFs.



**Fig. S11.** Tet photocatalytic degradation activity with the addition of radical scavengers, p-benzoquinone, triethanolamine and ethanol.
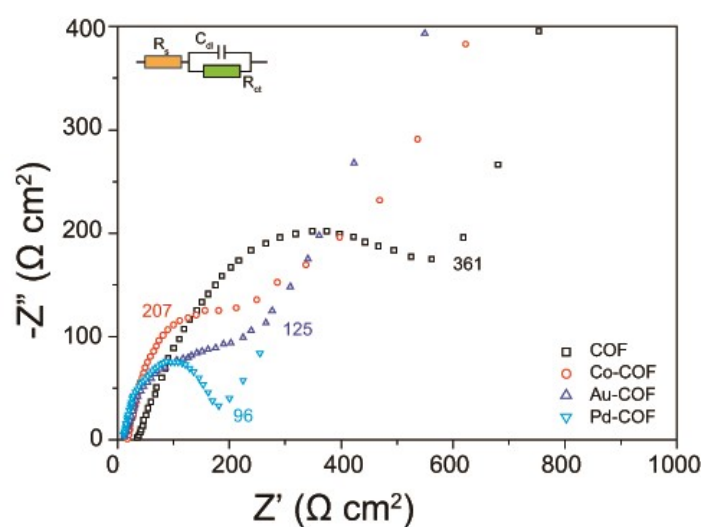


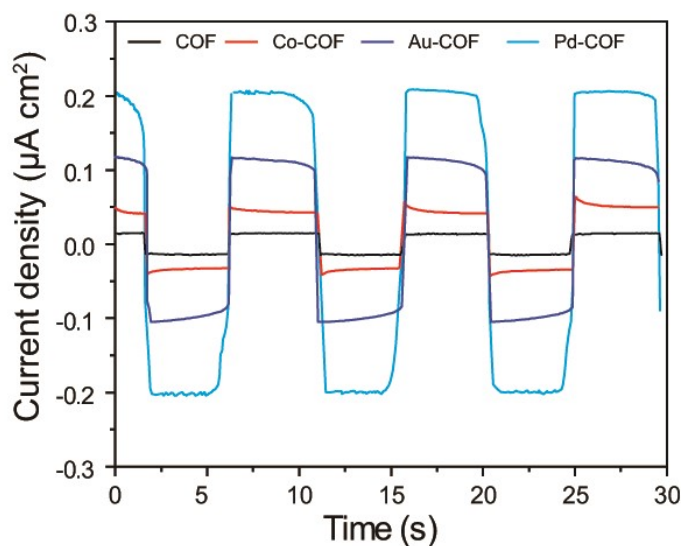**Fig. S12**. EIS plots of COFs, Co-COFs, Au-COFs and Pd-COFs.

**Fig. S13.** Transient photocurrent responses of COFs, Co-COFs, Au-COFs and Pd-COFs.

**Table S1**. Inductively coupled plasma mass spectrometry measurements on metal content in Me-COFs, Errors were obtained from 3 repeated experiments.

| Samples | Sample weight | Concentrations (mg/L) in 10 mL | Wt.% | %Error |
|---------|---------------|--------------------------------|------|--------|
| Pd-COF | 0.0013 | 4.8633 | 3.741 | 3.38 |
| Au-COF | 0.0012 | 3.0132 | 2.511 | 3.55 |
| Co-COF | 0.0011 | 6.9498 | 6.318 | 3.43 |

Parameters: RF Power：1.50KW, RF Matching：1.80V, Auxiliary flow：1.50L/min, Carrier Gas：1.10L/min, Omega Bias：-105V, Omega Lens：10.1V, Cell Entrance：-45V, Deflect：3.8V, Cell Exit：-62V, Plate Bias -60V.

[1]. Liu, G., Hou, G., Mao, X., Qi, X., Song, Y., Ma, X., Wu, J., Luo, G., Yao, H., Liu, Q., Chem. Eng. J 431 (2022) 133254.

[2]. Zhang, Z.; Wu, P.; Chen, L.; Wang, J., Appl. Phys. Lett. 2010 96, 232906.

[3]. Agarwal, V.; Metiu, H., J. Phys. Chem. C 2016, 120, 2320.