

Supporting Information

Noble Metal Sites Modulated Cyano-COF for Boosted Photocatalytic O₂ to H₂O₂ Production

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S1. Materials and Methods

All commercially available reagents and solvents were used as received without further purification, unless noted otherwise. 1, 3, 5-tris(*p*-formylphenyl)benzene ($C_{27}H_{18}O_3$, 97%), 1, 4-phenylenediacetonitrile ($C_{10}H_8N_2$, 97%), cesium carbonate (Cs_2CO_3 , 99.9%), platinum chloride ($PtCl_2$, 99%), palladium acetate ($Pd(OAc)_2$, 99%), silver nitrate ($AgNO_3$, 99.8%), and chloroauric acid ($HAuCl_4$, 98%) were commercially from Energy Chemical. Sodium phosphate dibasic (Na_2HPO_4 , $\geq 99.0\%$), sodium dihydrogenorthophosphate (NaH_2PO_4 , $\geq 99.0\%$), *p*-benzoquinone (BQ, 98%), *tert*-butanol (TBA, 99.5%), *N, N*-diethyl-*p*-phenylenediamine sulfate (DPD), sodium borohydride ($NaBH_4$, $\geq 98.0\%$) and potassium iodate (KIO_3) were supplied by Adamas Reagent Co., Ltd. Ethanol ($EtOH$, $\geq 99.7\%$) was purchased by Tianjin Yongda Chemical. Peroxidase (POD) was supplied by Sangon Biotech. Methyl Alcohol ($MeOH$, $\geq 99.5\%$) was purchased by General Reagents.

The powder wide angle X-ray diffraction pattern (PXRD) was recorded on a D/max-2300 diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The FT-IR spectra were obtained from Nicoletis10 FT-IR. N_2 adsorption-desorption isotherm was measured by ASAP 2460 analyzer. The samples were heated at $120^\circ C$ and kept at this temperature for 12 h under vacuum for activation. Ultra-high purity grade (99.999 % purity) N_2 was used for all free space corrections and measurements. Transmission electron microscopy (JEOL JEM-2100F) was utilized to observe the Pt/cyano-COF, Pd/cyano-COF, Au/cyano-COF and Ag/cyano-COF. The valence states of photocatalytic materials were evaluated by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD). Photoluminescence (PL) spectra were recorded using a Lengguang F97 Pro system. Electron paramagnetic resonance (EPR) signals were obtained at room temperature using DMPO as the trapping agent on an EPR200-plus spectrometer.

The photoelectrochemical test was performed on a three-electrode system using a computer-controlled electrochemical workstation (CHI 660F). Typically, 10 mg photocatalyst was ultrasonically dispersed in 500 μL of H_2O to form a homogeneous

suspension. Then, 10 μL suspension was evenly coated on the conductive side of the conductive glass (ITO) substrate and dried naturally. The three-electrode system consisted of an Ag/AgCl reference electrode, a Pt counter electrode, and the prepared sample as the working electrode. The electrolyte was 0.2 M Na_2SO_4 solution.

H_2O_2 concentration was determined by the DPD-POD method. Scavenger experiments were carried out by adding tert-butanol (TBA), *p*-benzoquinone (BQ), and potassium iodate (KIO_3) as scavengers for $\cdot\text{OH}$, $\cdot\text{O}_2^-$, and e^- , respectively.

S2. Characterization and Photocatalytic Performance

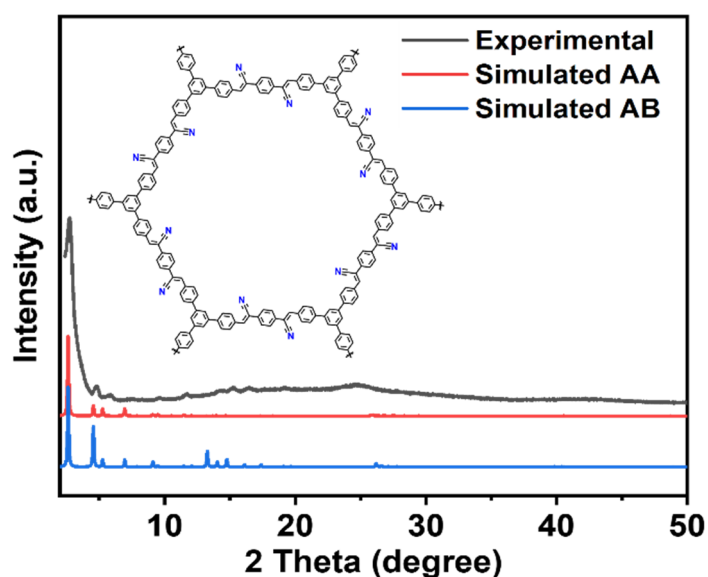


Figure S1. XRD pattern of cyano-COF.

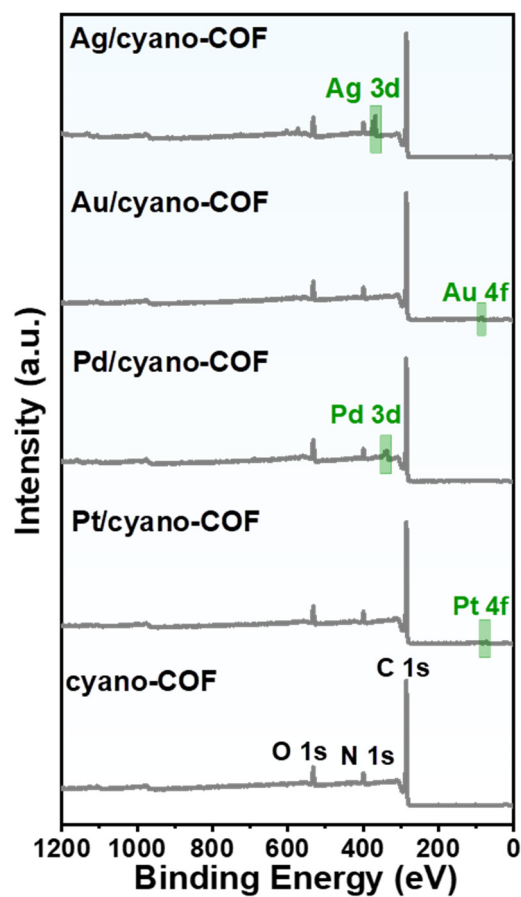


Figure S2. Wide scan XPS spectra of cyano-COF and metal/cyano-COF.

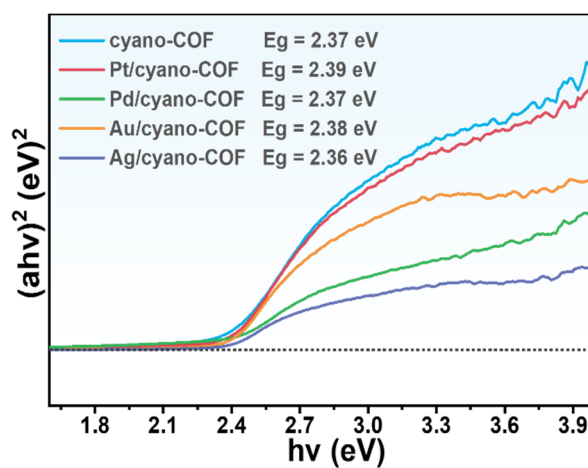


Figure S3. Tauc plots of cyano-COF and metal/cyano-COF.

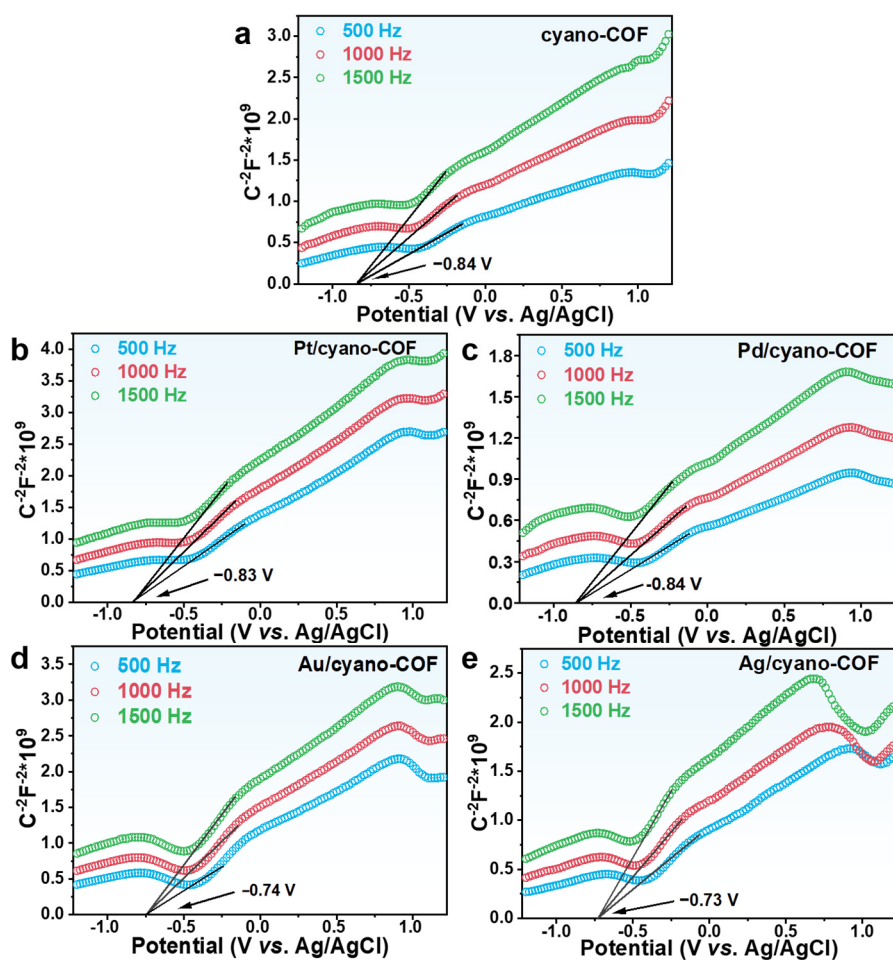


Figure S4. Mott-Schottky curves of cyano-COF and metal/cyano-COF.

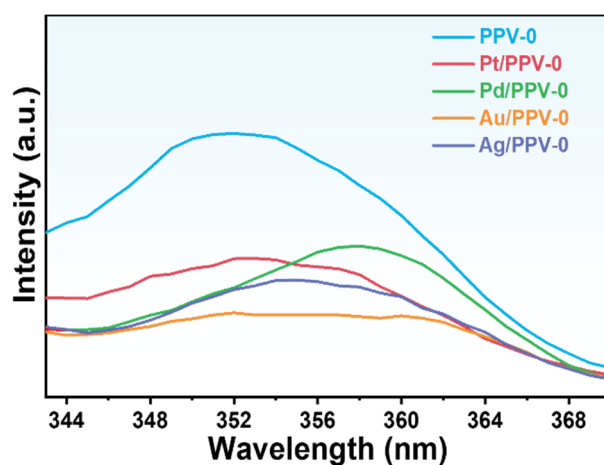


Figure S5. Photoluminescence spectra of cyano-COF and metal/cyano-COF.