

Electronic Supplementary Information

Ultrafine Platinum Nanoparticles Confined in a Covalent Organic Framework for Enhanced Enzyme-mimetic and Electrocatalytic Performances

Li Zhang^{1,†}, Chaoqin Han^{1,†}, Pu Zhang², Wensheng Fu¹, Yao Nie^{1,*}, and Yi Wang^{1,*}

¹ *Chongqing Key Laboratory of Green Synthesis and Applications, College of Chemistry, Chongqing Normal University, Chongqing 401331, P. R. China*

² *Chongqing Research Center for Pharmaceutical Engineering, College of Pharmacy, Chongqing Medical University, Chongqing 400016, China*

† These authors contributed equally to this work.

** Corresponding author. E-mail address: ywang@cqu.edu.cn (Y. Wang); nieyao@cqu.edu.cn (Y. Nie)*

Synthesis of unsupported platinum nanoparticles (Pt NPs)

Unsupported Pt NPs were synthesized according to a previously reported work with slight modification¹. In general, 555 mg of polyvinylpyrrolidone ($M_w \approx 55000$) were dissolved in 44 mL of deionized water. Then, 5 mL of chloroplatinic acid hexahydrate solution ($H_2PtCl_6 \cdot 6H_2O$, 25 mM) was added into the above solution. After stirring for 2 h, 1 mL of freshly prepared iced sodium borohydride solution (2.5 M) was quickly injected into the mixture under vigorous stirring. The reaction solution was dialyzed for two days, and the remaining dark solid phase was dried at 45°C under vacuum, which was collected as Pt NPs.

Synthesis of COF-Pt (physical mixture of COF and Pt NPs)

Briefly, 10 mg of TPB-DMTP-COF powder, 25.9 mg of above unsupported Pt NPs and 30 mg of polyvinylpyrrolidone ($M_w \approx 55000$) were dissolved in a mixed solvent containing 5 mL of ethanol and 5 mL of deionized water. The mixture was stirred for 15 h at room temperature. After centrifuging at 10,000 rpm for 10 min and washing with a mixture of ethanol and deionized water (1:1 in volume) for three times, the solid was dried at 45°C under vacuum and was obtained as COF-Pt.

References

- 1 Y. K. Du, P. Yang, Z. G. Mou, N. P. Hua, L. Jiang, Thermal decomposition behaviors of PVP coated on platinum nanoparticles, *J. Appl. Polym. Sci.*, **2006**, 99 (1), 23-26.

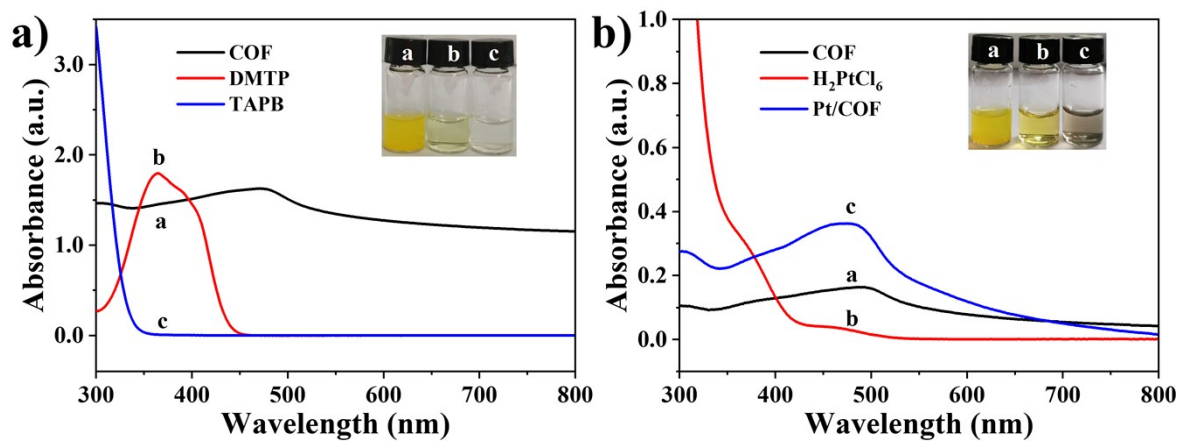


Figure S1 UV-vis absorption spectra and corresponding photograph (inset) of precursors/products in the synthesis of COF (a) and Pt/COF (b).

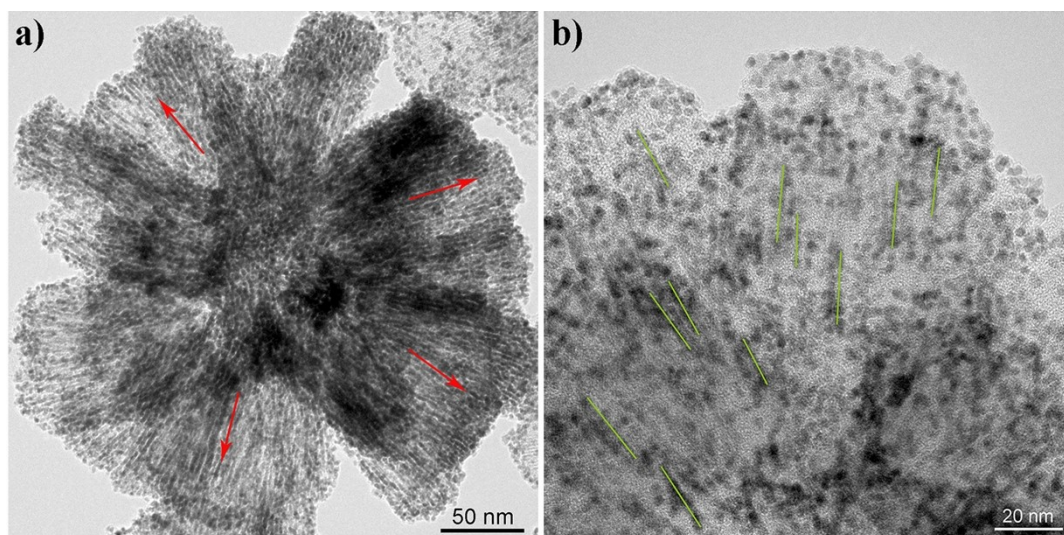


Figure S2 (a) and (b) TEM images of Pt/COF and Pt NPs in Pt/COF grow along a specific direction.

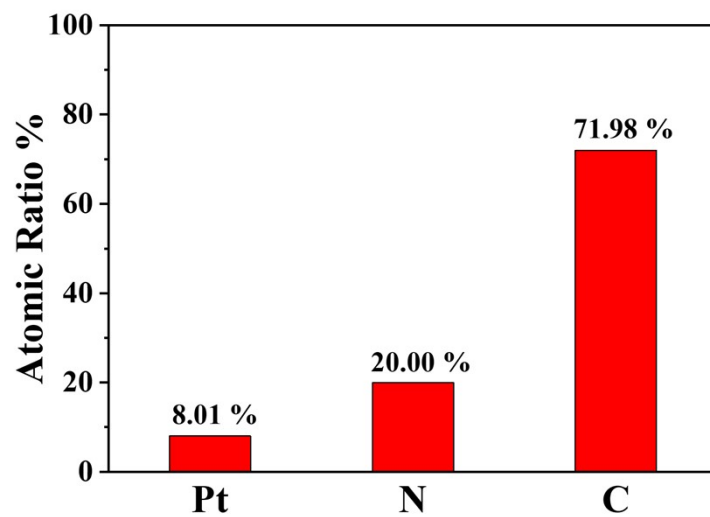


Figure S3 Atomic ratio of Pt, N, and C in Pt/COF measured by energy dispersive X-ray spectroscopy (EDS).

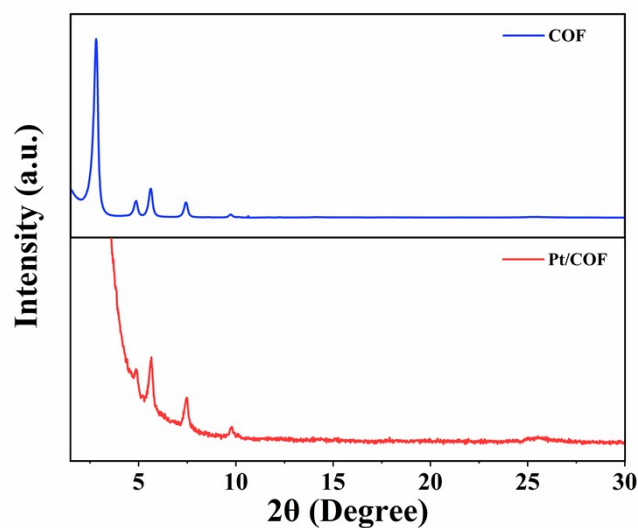


Figure S4 XRD patterns of COF and Pt/COF in the angle range of 1.5~30°.

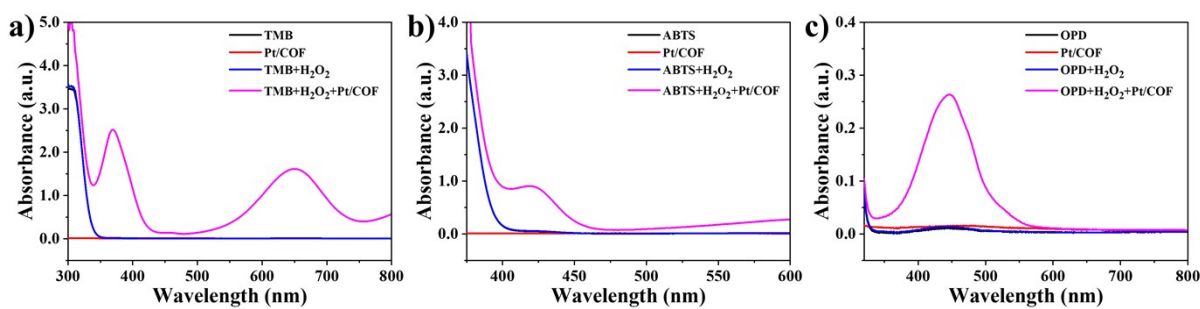


Figure S5 UV-vis spectra of different peroxidase substrates in the absence and presence of Pt/COF catalyst: (a) TMB + H₂O₂, (b) ABTS + H₂O₂, and (c) OPD + H₂O₂.

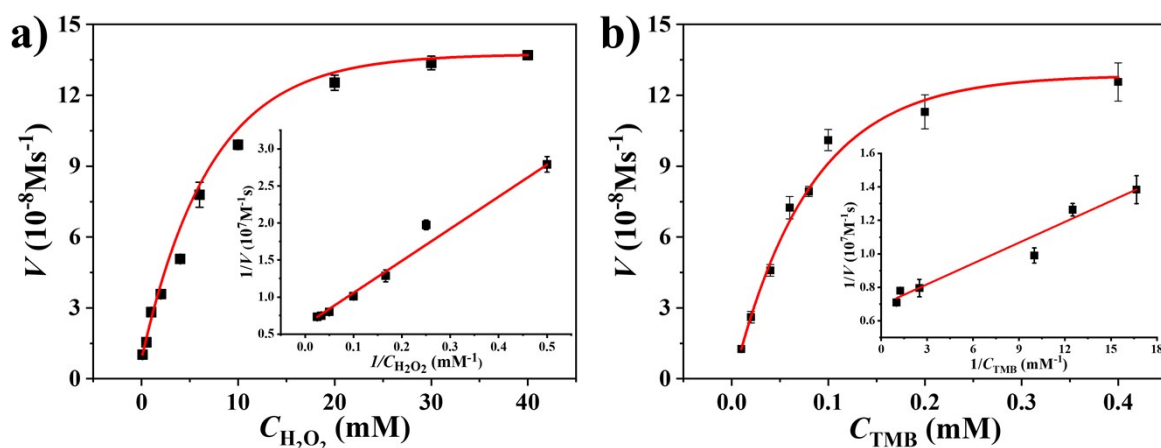


Figure S6 Steady-state kinetic assays of Pt/COF for catalytic oxidation of TMB by H₂O₂. The data were obtained by keeping experimental conditions constant but only varying the concentration of TMB or H₂O₂. The embedded graphs show the Lineweaver-Burk plots transformed from the Michaelis-Menten equations.

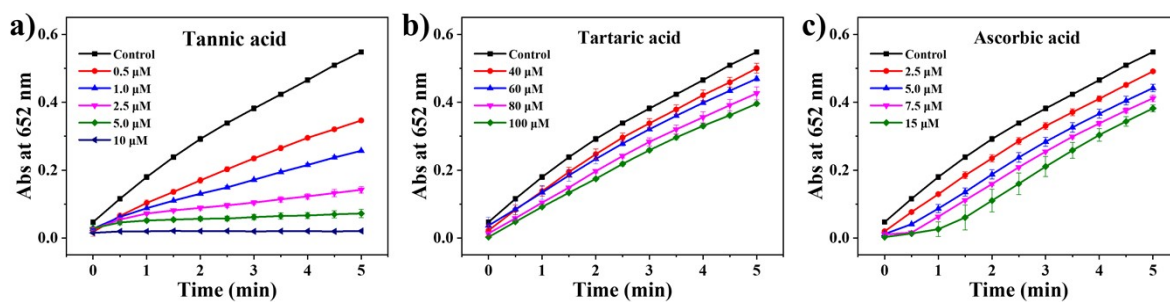


Figure S7 Kinetic curves showing the inhibition of different antioxidants on the catalytic oxidation of TMB as a function of reaction time: (a) tannic acid, (b) tartaric acid, and (c) ascorbic acid.

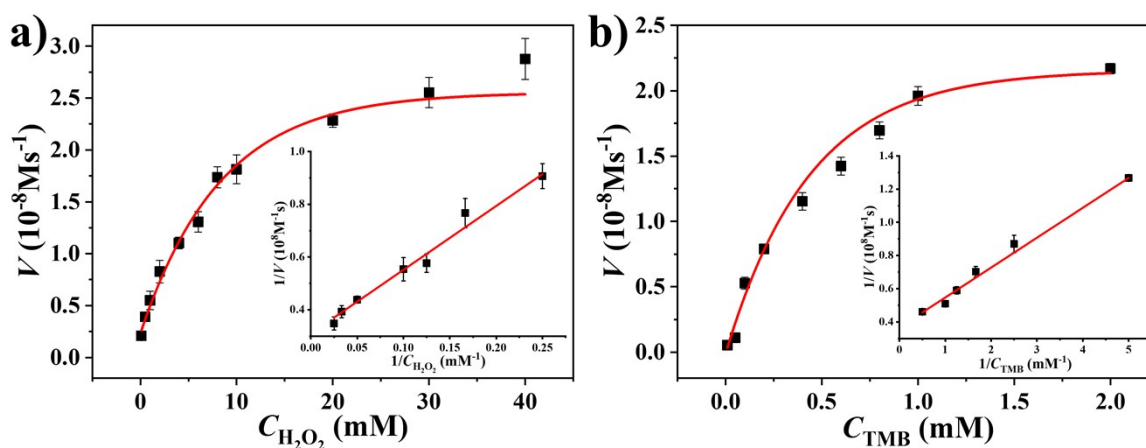


Figure S8 Steady-state kinetic assays of Pt/COF in the presence of tannic acid for catalytic oxidation of TMB by H_2O_2 . The embedded graphs show the Lineweaver-Burk plots transformed from the Michaelis-Menten equations.

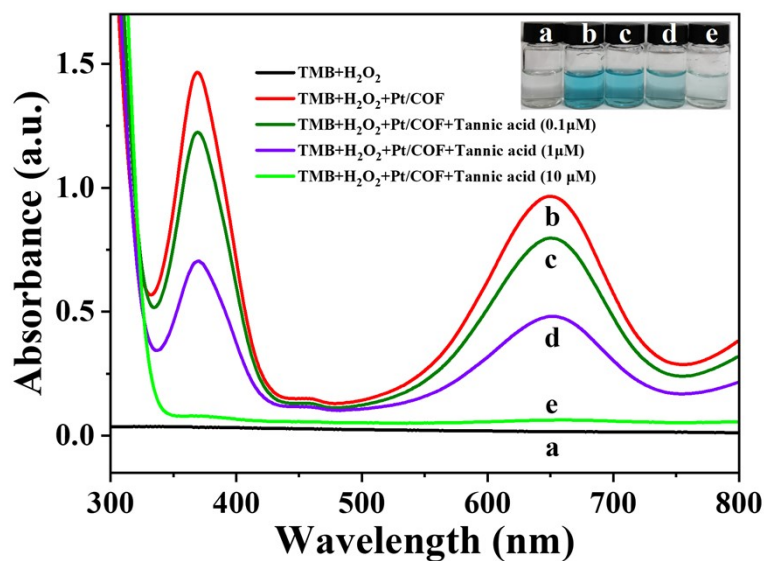


Figure S9 UV-vis absorption spectra and corresponding photograph (inset) showing the concentration-dependent inhibition effect of tannic acid on the catalytic oxidation of TMB by Pt/COF.

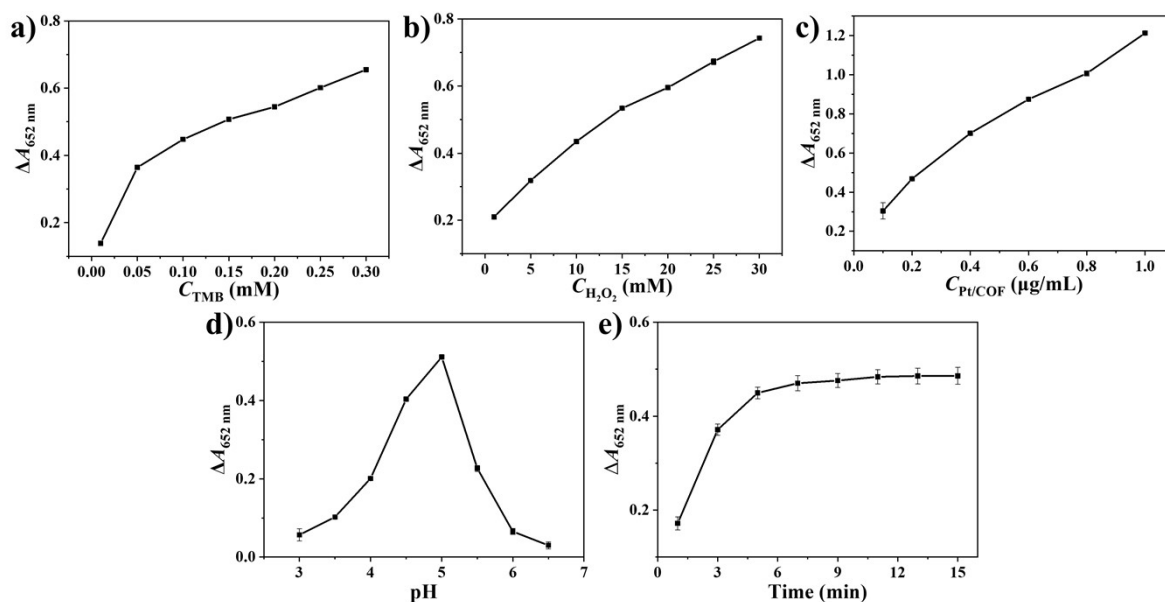


Figure S10 Absorbance change at 652 nm ($\Delta A_{652 \text{ nm}}$) of the reaction system under different conditions: (a) concentration of TMB, (b) concentration of H_2O_2 , (c) concentration of Pt/COF, (d) pH value, and (e) reaction time.

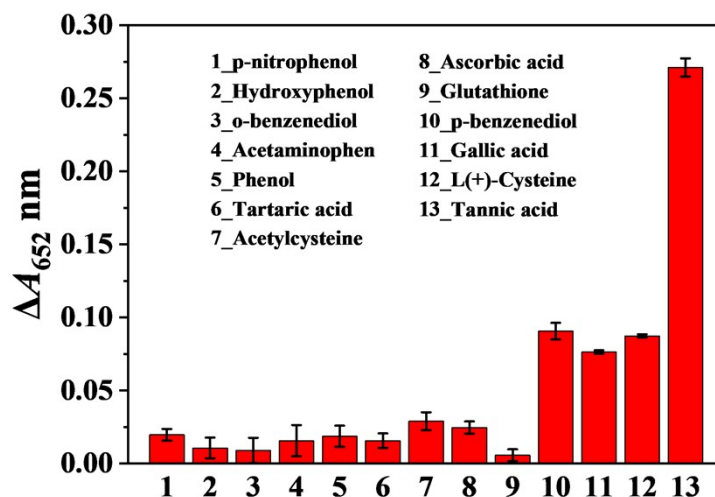


Figure S11 Selectivity of this method for tannic acid detection. The absorbance change at 652 nm (ΔA_{652} nm) of reaction solutions in the presence of tannic acid or other substances (1 ~ 13: p-nitrophenol, hydroxyphenol, o-benzenediol, acetaminophen, phenol, tartaric acid, acetylcysteine, ascorbic acid, glutathione, p-benzenediol, gallic acid, L(+)-cysteine, and tannic acid).

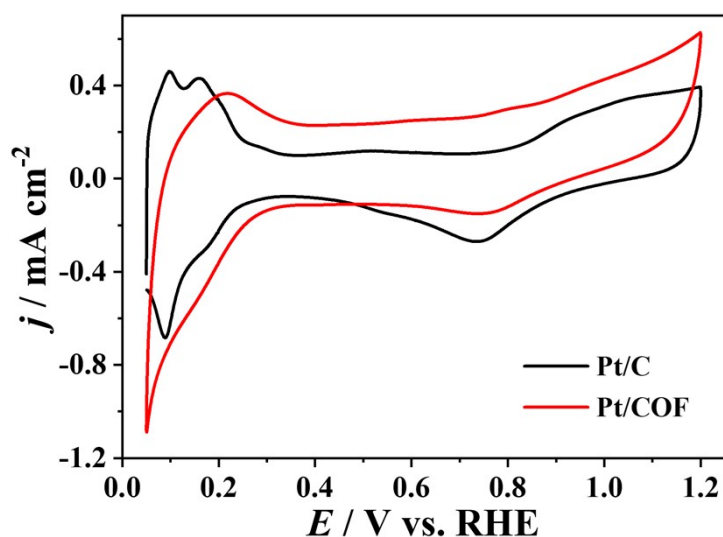


Figure S12 Cyclic voltammograms for Pt/COF and JM-Pt/C in N_2 -saturated 0.5 M H_2SO_4 solutions at a scan rate of 50 mV/s.

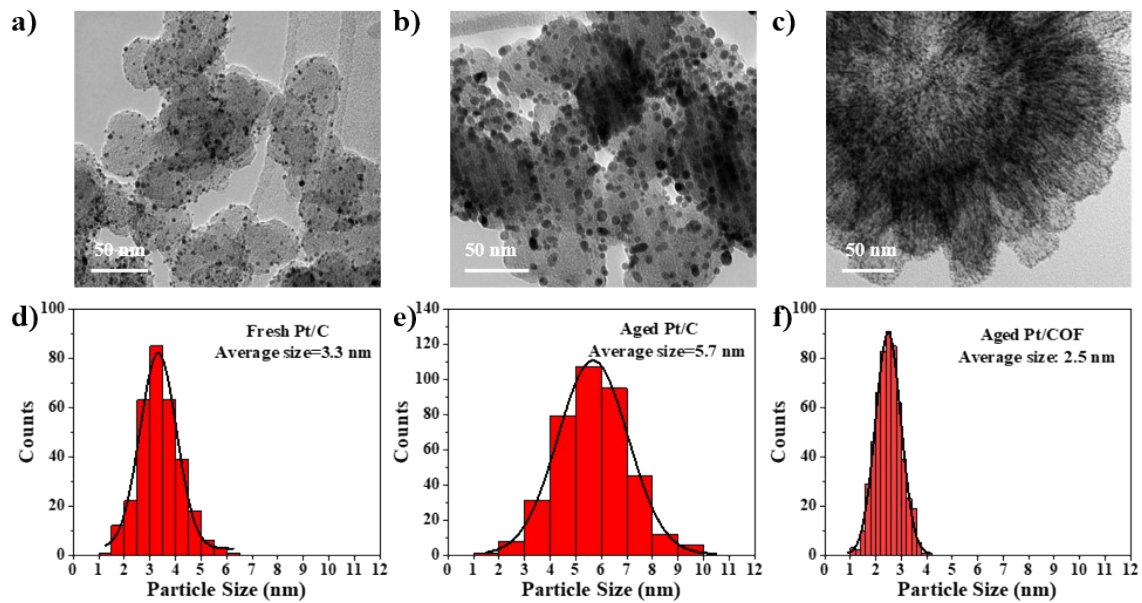


Figure S13 TEM image of (a) fresh Pt/C, (b) Pt/C after stability test, and (c) Pt/COF after stability test. Corresponding particle-distribution histograms of (d) fresh Pt/C, (e) Pt/C after stability test, and (f) Pt/COF after stability test.

Table S1 Comparison of the kinetic parameters of the present system toward the oxidation of TMB by H₂O₂.^a

Sample	Substrate	K_m (mM)	V_{max} (M s ⁻¹)
Pt/COF	H ₂ O ₂	6.94	1.6×10^{-7}
Pt/COF+ tannic acid	H ₂ O ₂	7.81	3.23×10^{-8}
Pt/COF	TMB	0.061	1.46×10^{-7}
Pt/COF+ tannic acid	TMB	0.49	2.72×10^{-8}

^a K_m is the Michaelis constant, and V_{max} is the maximal reaction velocity. Conditions: at 25 °C in a HAc-NaAc (0.2 M, pH 4.5) buffer.

Table S2 Results for the detection of tannic acid from different types of tea and the spiked recovery experiments.

Sample	Detected (μ M)	Spiked (μ M)	Found (μ M)	Recovery (%, n=3)	RSD (%, n=3)
Black tea	0.05	1.00	1.09	104.0	3.40
Green tea	0.16	1.00	1.14	98.0	4.90
Oolong tea	0.04	1.00	1.06	102.0	5.50