Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

2D Metal Chalcogenides with Surface Fully Covered by Organic "Promoter" for High-performance Biomimetic Catalysis

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Experimental Section

Characterization. The FT-IR spectra were recorded on a Bruker VERTEX70 FT-IR spectrometer in 4000–400 cm^{-1} region using KBr pellets. PXRD patterns were recorded on a Rigaku MiniFlex II diffractometer and a Rigaku Miniflex 600 diffractometer using Cu Kα radiation by keeping the powdered sample on a silicon substrate, from 5 to 65˚. UV-Vis absorption was performed with a Lambda 950. TEM images were obtained on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV. Atomic force microscopy (AFM) measurements were performed using Bruker dimension ICON scanning probe microscope with Peakforce tapping mode. The surface chemical analysis was investigated by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific ESCALAB 250 Xi XPS system. A low power sonic baths was used KQ5200DE (200W, 40 kHz), from Kunshan Ultrasonic Instrument. Co., LTD, China; Centrifugation was carried out using a TGL-16C centrifuge from Shanghai Anting Scientific Instrument Factory, China. Glucose and perox ide (30%, H_2O_2), acetic acid (HAc), sodium acetate (NaAc) and Sodium hydroxide (NaOH) were purchased from Beijing Chemical Reagent Co. (Beijing, China). 3,3’,5,5’-Tetramethylbiphenyl dihydrochloride (TMB·HCl2) was purchased from Solarbio (Beijing, China), Glucose oxidase (GOx, 50KU) was purchased from Sigma-Aldrich and stored at -18 °C. All reagents were of analytical reagent grade, and used as received.

Materials and Reagents.

All reagents were purchased commercially and used without further purification.

4-Hydroxythiophenol (97 %) was purchased from Aladdin. Whereas, 4-Mercaptobenzoate (90 %) was purchased from Adamas Reagent, Ltd. China. Silver nitrate (AR, ≥ 99.8 %), Sodium hydroxide (AR, ≥ 96.0 %), Copper (Ⅱ) chloride dehydrate (AR, ≥ 99.0 %) and Copper (I) oxide (AR, 97.0 %), were purchased from Aladdin. Acetonitrile (AR, ≥ 99.0 %), and Ethanol (AR，≥ 99.7 %) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Water was purified using the Milli-Q purification system. Hydrogen chloride (AR，36.0～38.0%, *w* %) was purchased from Sinopharm Chemical Reagent Co., Ltd, China.

Synthesis of CuHBT. 4-Hydroxythiophenol (0.0437 g, 0.346 mmol) and $CuCl_2 \cdot 2H_2O$ (0.0145 g, 0.085 mmol) were dissolved in EtOH (5 mL) in room temperature. The mixture was sonicated for 2 h at 40 °C. When all the reactants were reacted into a viscous yellow compound, then 1.25 M HCl (0.5 mL) was drop added into the viscous yellow compound. The mixture solution was then sonicated for another 1 h, giving a yellow liquid crystal-like solution. Let yellow solution sit for a day. Then a dropper pipette was used to absorb the liquid supernatant, and then the liquid supernatant was centrifuged for 30 minutes at 2000 rpm. Finally, the top 2/3 liquid supernatant was retained as the finally products after centrifuging

Synthesis of CuMBA. Cu_2O (0.0210 g, 0.147 mmol) and 4-Mercaptobenzoate (0.0677 g, 0.439 mmol) were mixed in water (5 mL) at room temperature, then 12 M HCl was drop added into the turbidity solution. Then the mixture was sonicated for 30 min. The solution was then heated to 85 ^oC for 5 days in the oven and gave pale yellow sheet-like nanosheets. The pale yellow nanosheets were washed with ethanol, water, ethanol and finally diethyl ether. Then the CuMBA nanosheets were collected by suction filtration and dried under vacuum at 70 ^oC overnight. Finally, CuMBA (1 mg / mL) in 10 mL vial was sonicated with 200 W output power for 60 minutes in water, then centrifugation the solution at 5000 rpm for 30 min. The top of 2/3 was collected by pipette.

Synthesis of AgHBT. 4-Hydroxythiophenol (0.1095 g, 0.868 mmol), $AgNO_3$ (0.0210 mg, 0.124 mmol) were dissolved in water (5 mL) in room temperature, then cautiously add, dropwise triethylamine (as base), allowing the reaction to subside and again wobble between drops. Then the mixture was sonicated for 30 min. Later, the reactor was heated at 85 ^oC for 3 days and then allowed to cool to room temperature. The silver nanosheets were obtained, washed with ethanol, water, ethanol and finally diethyl ether then dried under vacuum at 70 ^oC overnight. Sonication AgHBT (10 mL EtOH in a 20 mL vial) with an initial concentration of 3 mg/mL in a sonic bath at power output of 200 W for 60 min. Centrifugation at 2000 rpm for 30 minutes. The top of 2/3 was collected by pipette.

Crystal structures. The crystal structure of AgHBT was firstly created based on the structure model of CuHBT, and then the cell parameters were refined against PXRD patterns via Le Bail refinements using the Jana package.[1] Finally, the geometry optimization calculations based on density functional theory (DFT) were performed to get precise positions of all atoms in their structures using the CASTEP module implemented in the Materials Studio package.[2-3] Based on its PXRD reflections, AgHBT have a orthorhombic unti cell as $a= 30.278$ Å, $b= 5.122$ Å, $c=3.983$ Å, $\alpha=\beta=\gamma=90^o$, $R_p = 9.37$, $R_{wp} = 13.83$, GOOF = 1.63. AgHBT is structurally analogous to CuHBT and CuMBA.[4-5] AgHBT possesses a two dimensional $\{AgS\}_n$ layer in which phenol motifs extend perpendicular to both side of the continuous metal chalcogenide.

H_2O_2 detection. H_2O_2 detection was carried out as follows: 30 μL of TMB (8 mM), 15 μL of CuHBT (0.5 mg/mL) stock solution were added to 135 μL of H_2O_2 with different concentrations. The mixed solution was used to perform the time course measurement at the wavelength of 652 nm.

Glucose detection. Firstly, 50 uL of glucose with various concentrations and 10 uL of GOx (15 mg mL^{-1}) were incubated at 37 ^oC in HAc-NaAc buffer (50 μL, pH 4.5) for 40 min; then 30 μL TMB (8 mM), 15 μL of the catalyzer (0.5 mg mL^{-1}), and 135 μL of H_2O were added into the above mixed solution; subsequently, the time course measurement was performed on microplate reader (Tecan Infinite 200 Pro, TECAN, Switzerland) at λ=652 nm.

Steady-state kinetic assay. Steady-state kinetic assays for peroxidase-like activity were carried out by measuring the absorbance change of the CuHBT/TMB/H_2O_2 system at 652 nm for 10 min. Experiments were performed at 37 °C, using 0.5 mg L^{-1} CuHBT in a reaction volume of 50μL 100 mM acetate buffer solution (pH 4.5) with 8.0 mM TMB as the substrate, and H_2O_2 was 100 mM. TMB was added to start the reaction, prior to recording the absorbance. The apparent kinetic parameters were calculated based on the Michaelis equation $\nu = V_{max} \times [S]/(K_m + [S])$, where ν is the initial velocity, V_{max} is the maximal reaction velocity, [S] is the concentration of the substrate, and K_m is the Michaelis–Menten constant.

Results and discussion

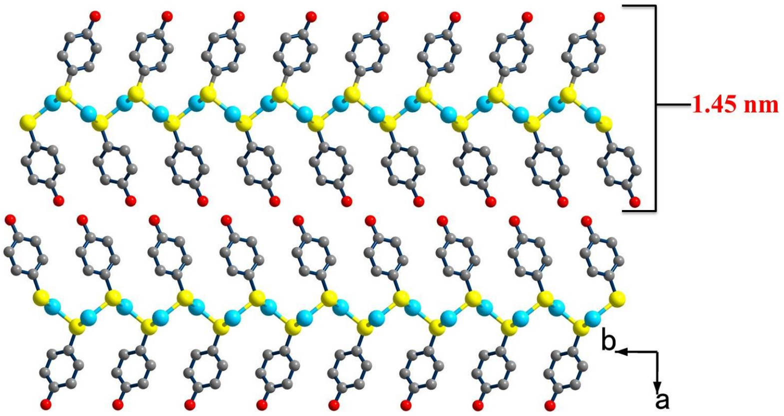

Fig. S1. Stacking mode of CuHBT structure, thickness of the single layer is about 1.45 nm.

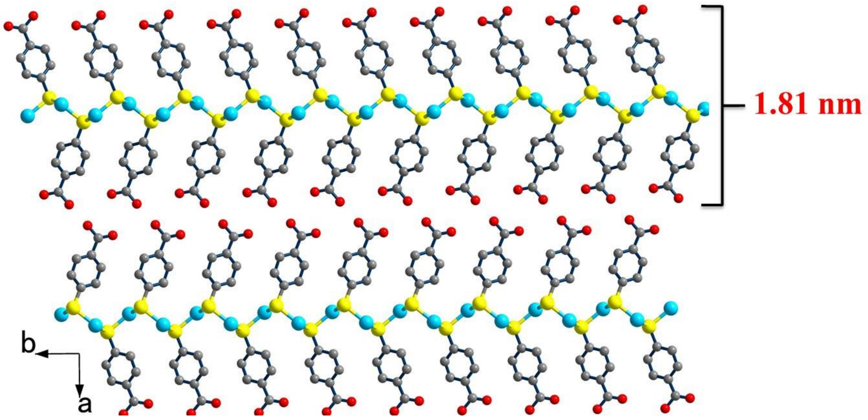

Fig. S2. Stacking mode of CuMBA structure, thickness of the single layer is about 1.81 nm.

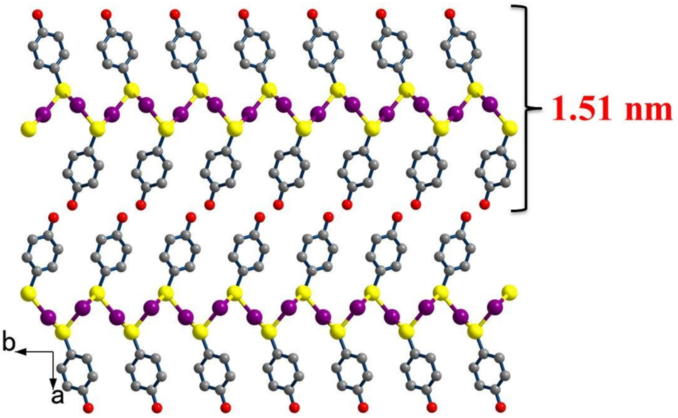

Fig. S3. Stacking mode of AgHBT structure, thickness of the single layer is about 1.51 nm.

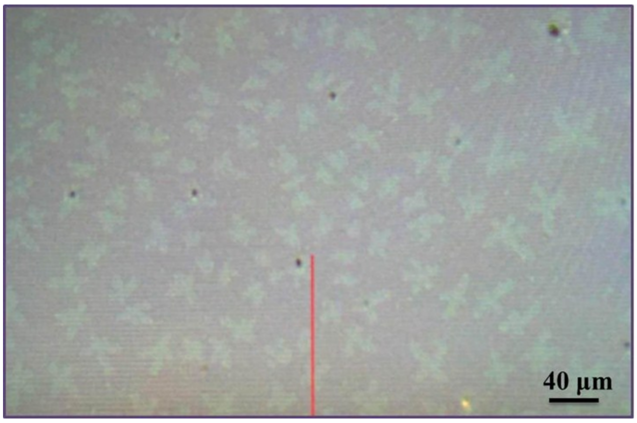

Fig. S4. Photograph of CuHBT on the Si/SiO$_2$ substrate.

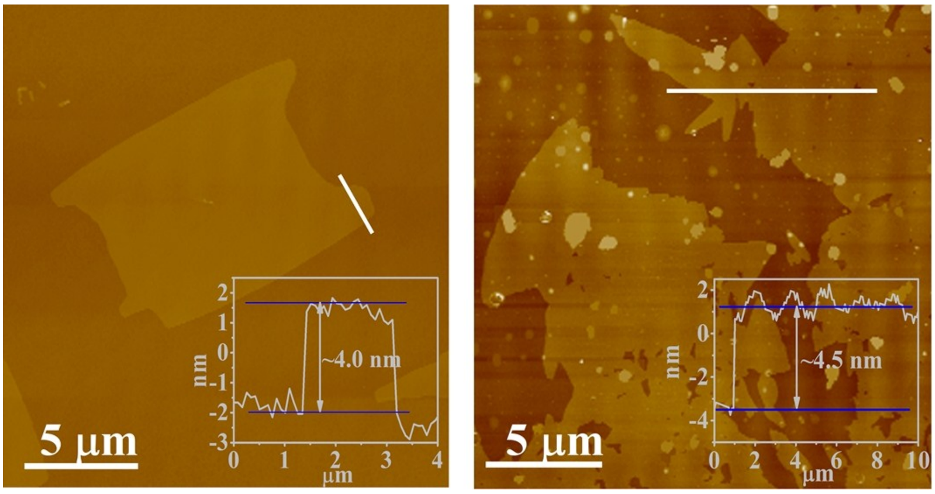

Fig. S5. AFM of CuMBA (**a**), and AgHBT (**b**) on SiO$_2$/Si substrate.

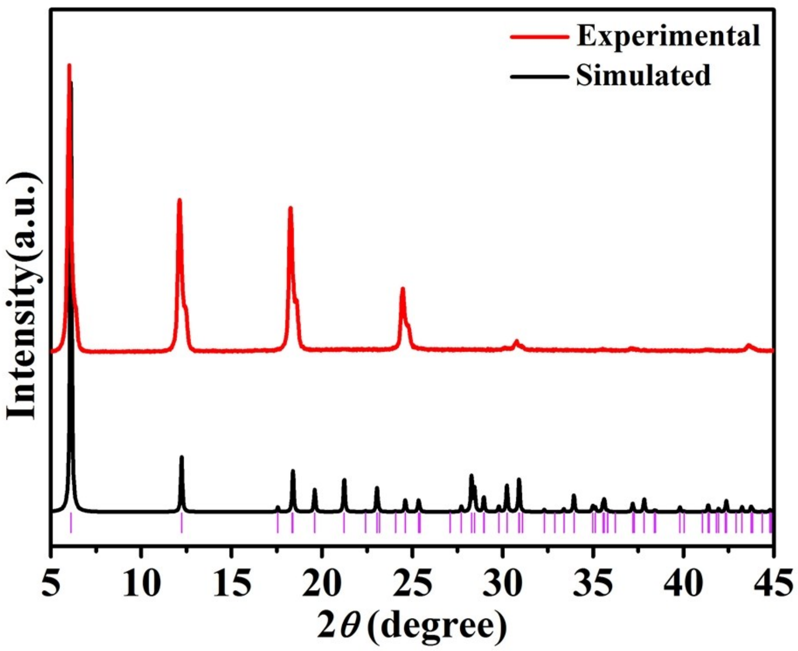

Fig. S6. PXRD patterns of CuHBT and its simulated one.

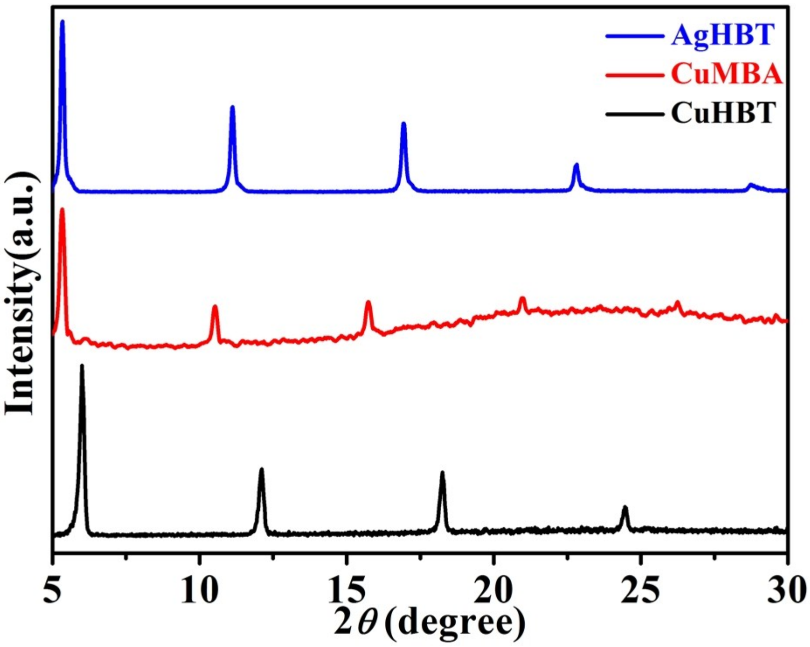

Fig. S7. PXRD patterns of CuHBT, CuMBA, and AgHBT on SiO_2/Si substrate.

Fig. S8. Photographs of the compared colorimetric reactions of CuHBT, CuMBA and AgHBT.

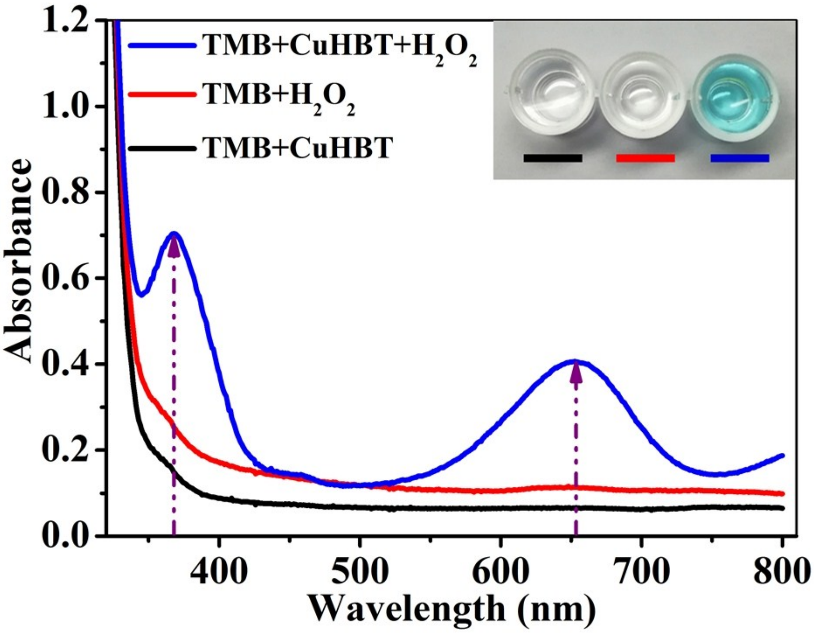

Fig. S9. Time-dependent absorbance changes at 652 nm of TMB in different reaction systems: CuHBT+TMB (black line); TMB+H_2O_2 (red line); TMB+H_2O_2+CuHBT (blue line).

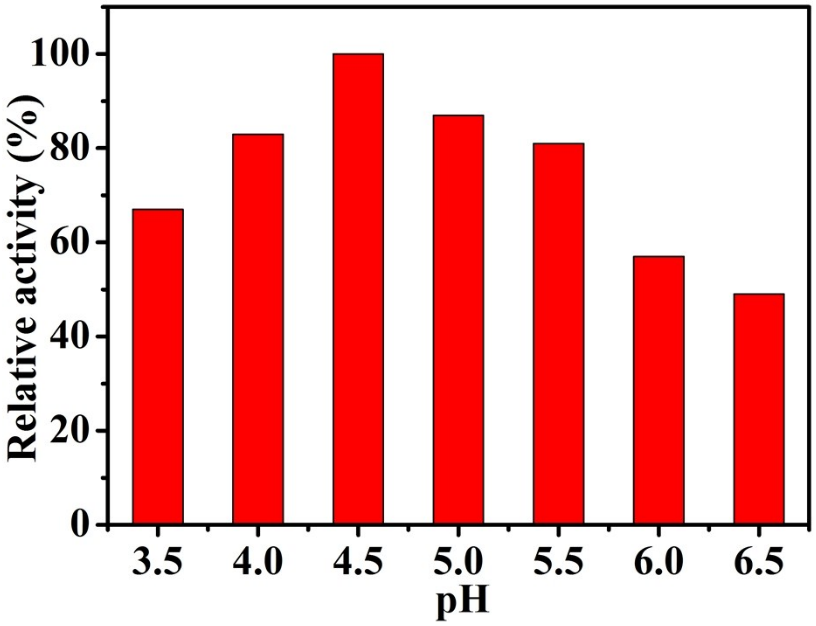

Fig. S10. pH dependent peroxidase-like activity of CuHBT.

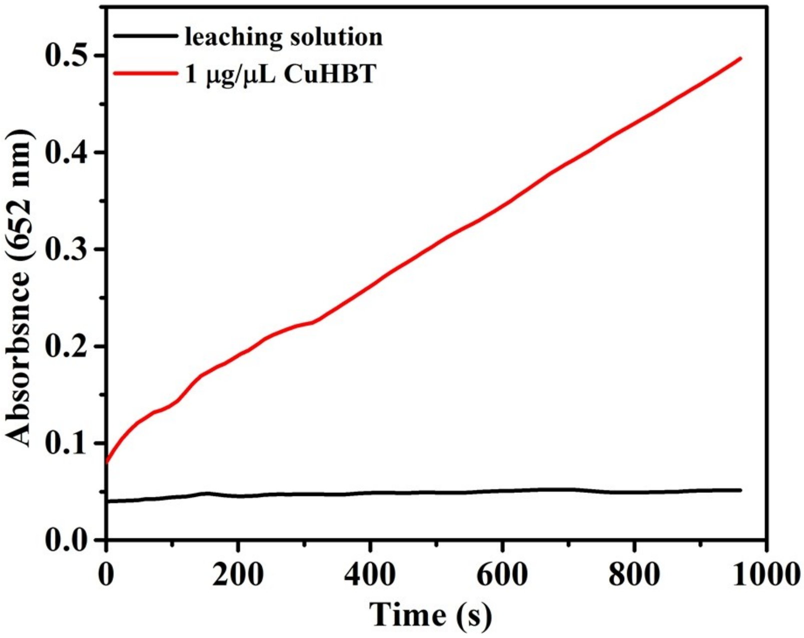

Fig. S11. Compare of time-dependent absorbance of CuHBT and its leaching solution.

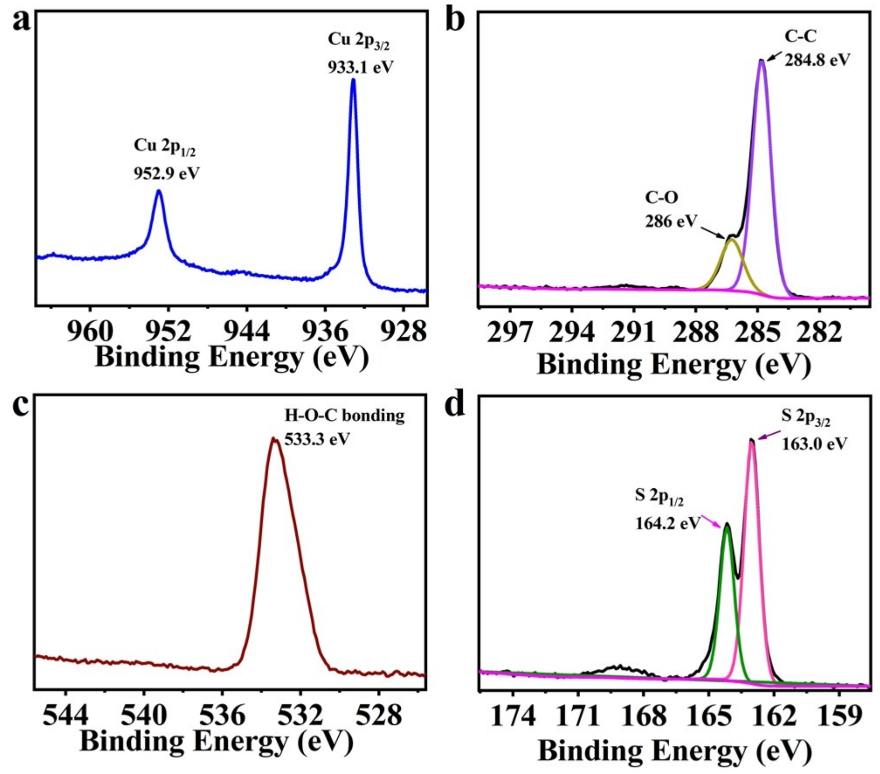

Fig. S12. XPS data of CuHBT after catalyst reaction.

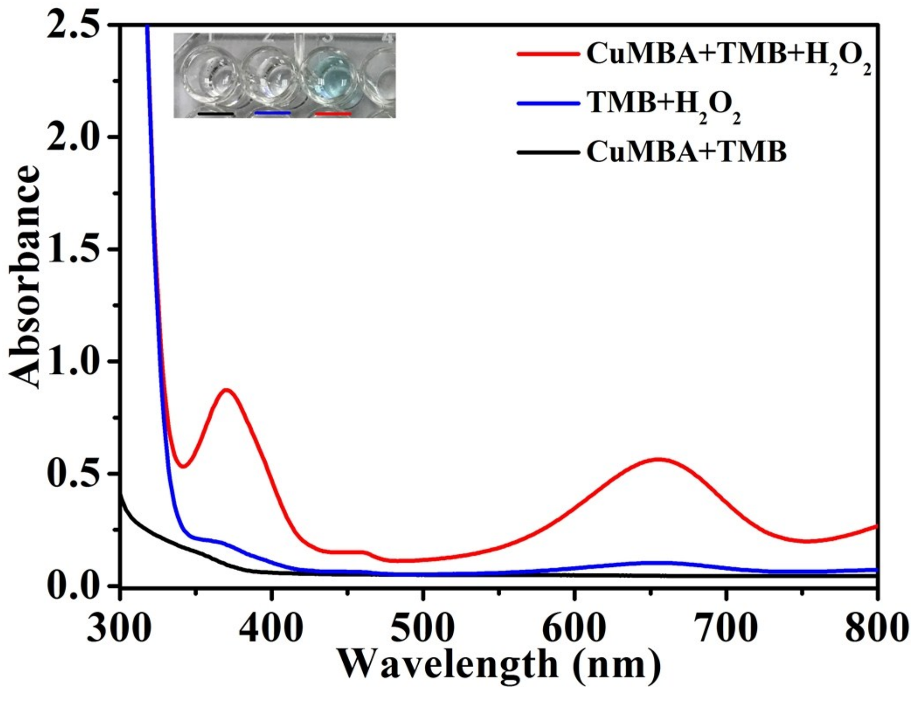

Fig. S13. Time-dependent absorbance changes at 652 nm of TMB in different reaction systems: CuMBA+TMB (black line); TMB+H_2O_2 (blue line); TMB+H_2O_2+CuMBA (red line).

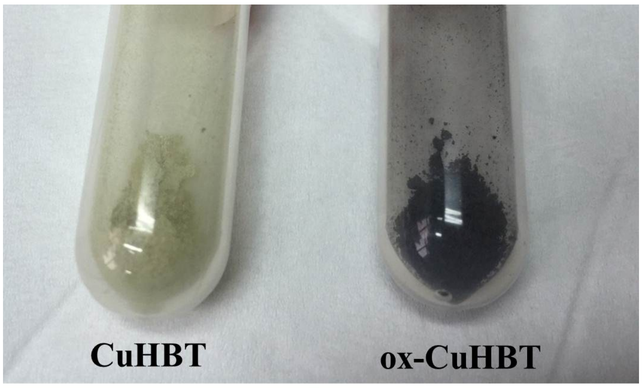

Fig. S14. Photographs of collected and dried CuHBT and ox-CuHBT.

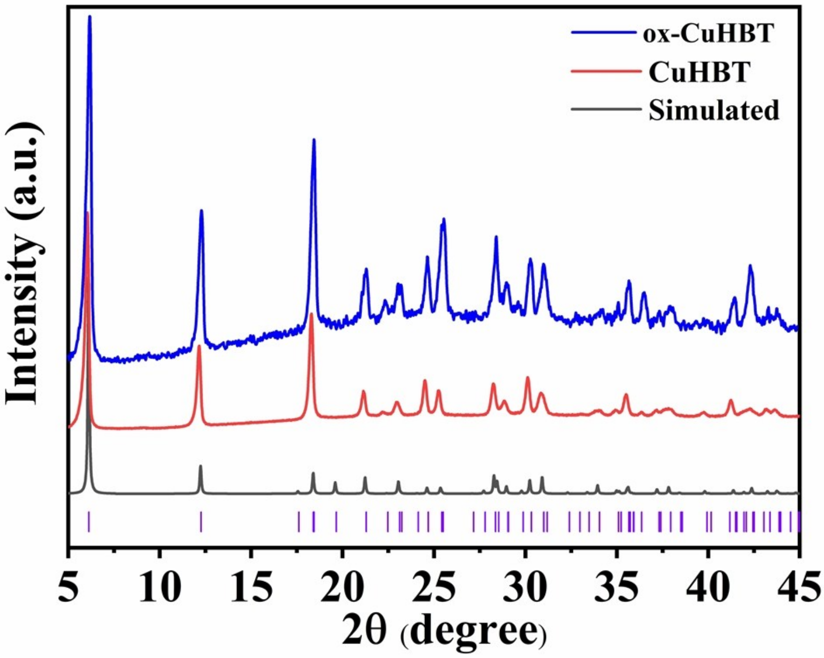

Fig. S15. PXRD patterns of CuHBT and ox-CuHBT.

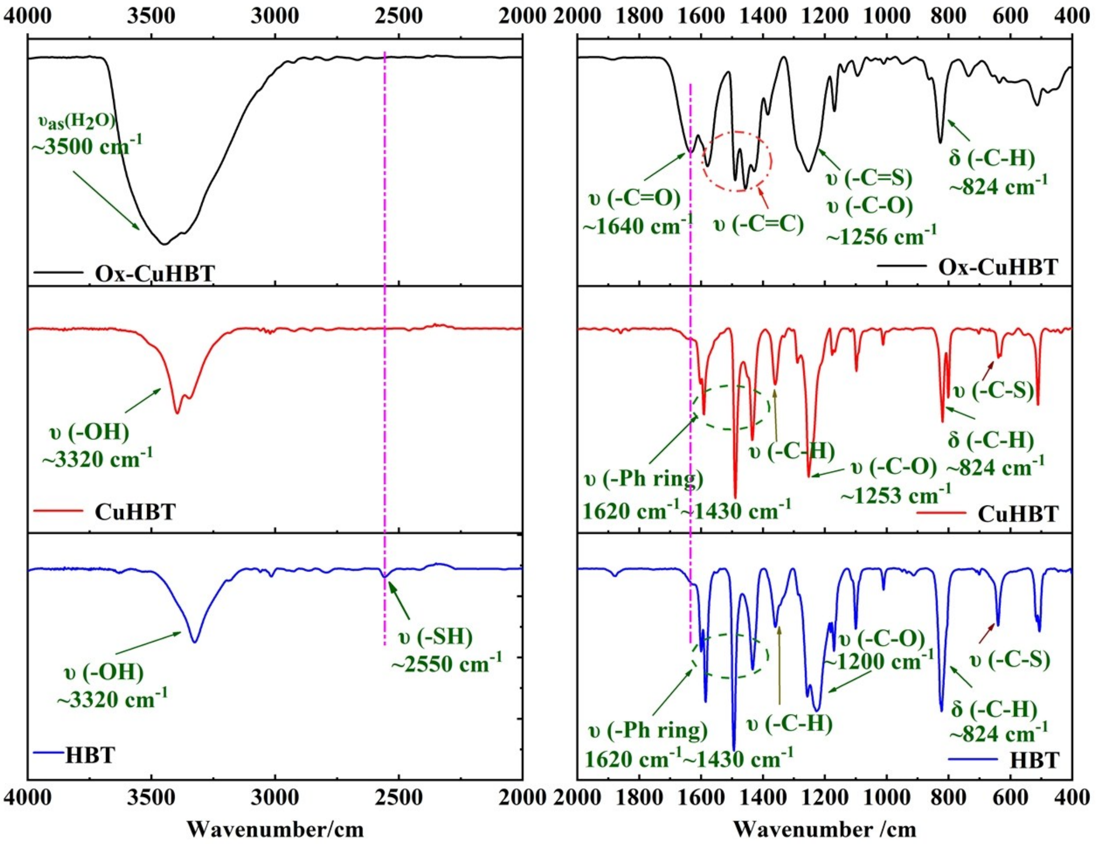

Fig. S16. FTIR spectra of HBT, CuHBT and ox-CuHBT.

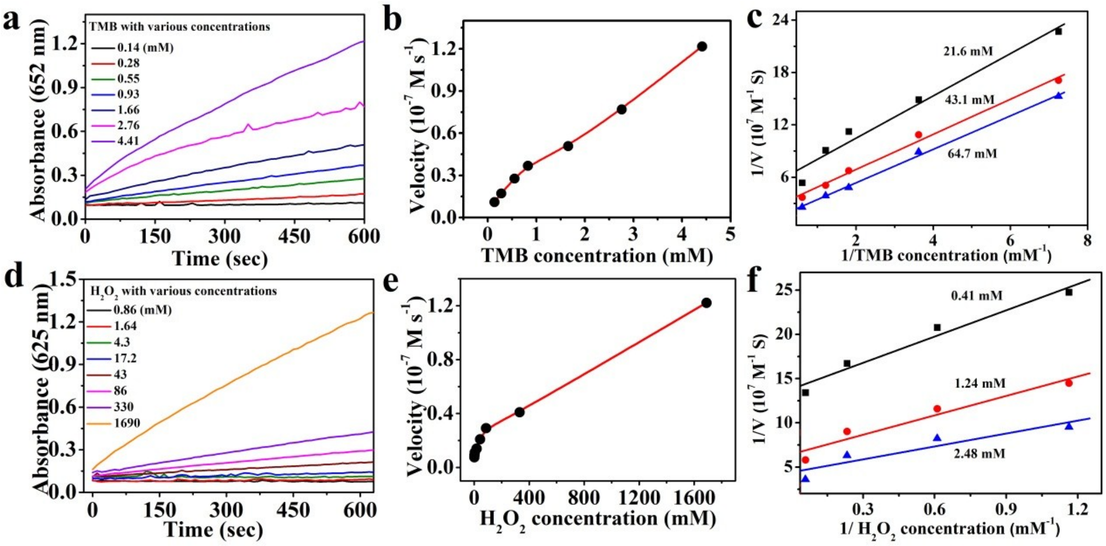

Fig. S17. Steady-state kinetic assay and catalytic mechanism of CuHBT nanosheets. The velocity (v) of the reaction was measured using 15 μL CuHBT in 50 μL of 100 mM acetate buffer (pH 4.5) at room temperature. (a) The corresponding time dependent absorbance changes of apparent steady-state kinetic study in the presence of different concentrations of TMB; (b) The concentration of H_2O_2 was 21.6 mM and

TMB concentration was varied; (c) Double reciprocal plots of activity of CuHBT nanosheets with the concentration of H_2O_2 fixed and the TMB varied; (d) The corresponding time dependent absorbance changes of apparent steady-state kinetic study in the presence of different concentrations of H_2O_2; (e) The concentration of TMB was 0.41 mM and H_2O_2 concentration was varied ; (f) Double reciprocal plots of activity of CuHBT nanosheets with the concentration of one substrate TMB fixed and the H_2O_2 varied.

Reference

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