

Supporting Information

One-step synthesis of organotin-functionalized polyoxometalate@ZIF-67 composite: an effective non-enzymatic colorimetric acetone sensor

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Table S1 The molecular formula of $\text{PW}_9\text{-Zn}$, $\text{PW}_9\text{-TM-SnRCOO}$ and $\text{P}_2\text{W}_{15}\text{-TM-SnRCOO}$

molecular formula	abbreviation	Refs.
$\text{K}_{10}[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 41\text{H}_2\text{O}$	$\text{PW}_9\text{-Mn}$	41
$\text{K}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 22\text{H}_2\text{O}$	$\text{PW}_9\text{-Co}$	42
$\text{K}_{10}[\text{Zn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 22\text{H}_2\text{O}$	$\text{PW}_9\text{-Zn}$	42
$\text{Na}_{16}[\text{Mn}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 53\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{-Mn}$	43
$\text{Na}_{16}[\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 51\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{-Co}$	44
$\text{Na}_{16}[\text{Zn}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 50\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{-Zn}$	45
$\text{K}_{10}[\text{Mn}_2\{\text{Sn}(\text{CH}_2)_2\text{COO}\}_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 14\text{H}_2\text{O}$	$\text{PW}_9\text{-Mn-SnRCOO}$	47
$\text{Na}_3\text{K}_7[\text{Co}_2\{\text{Sn}(\text{CH}_2)_2\text{COO}\}_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 17\text{H}_2\text{O}$	$\text{PW}_9\text{-Co-SnRCOO}$	47
$\text{Na}_8\text{K}_2[\text{Zn}_2\{\text{Sn}(\text{CH}_2)_2\text{COO}\}_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2] \cdot 13\text{H}_2\text{O}$	$\text{PW}_9\text{-Zn-SnRCOO}$	47
$\{\text{C}(\text{NH}_2)_3\}_{12}\text{H}_4[\{\text{Sn}(\text{C}_3\text{H}_4\text{O}_2)_2\text{Mn}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2\}] \cdot 22\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{-Mn-SnRCOO}$	48
$\{\text{C}(\text{NH}_2)_3\}_{12}\text{H}_4[\{\text{Sn}(\text{CH}_2)_2\text{COO}\}_2\text{Co}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 14\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{-Co-SnRCOO}$	49
$\{\text{C}(\text{NH}_2)_3\}_{11}\text{H}_5[\{\text{Sn}(\text{CH}_2)_2\text{COO}\}_2\text{Zn}_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 13\text{H}_2\text{O}$	$\text{P}_2\text{W}_{15}\text{-Zn-SnRCOO}$	49

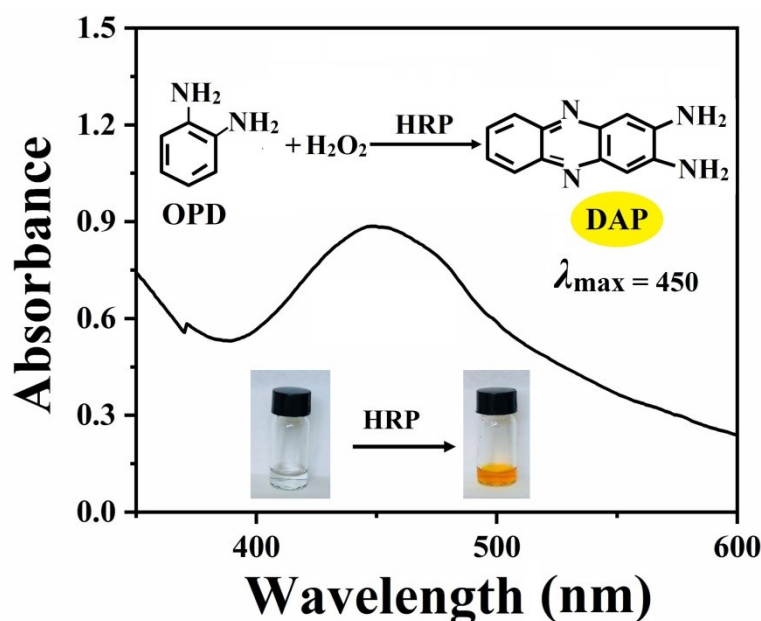


Fig. S1 UV-vis spectrum of the reaction solution of OPD catalyzed by HRP in the presence of H_2O_2 .

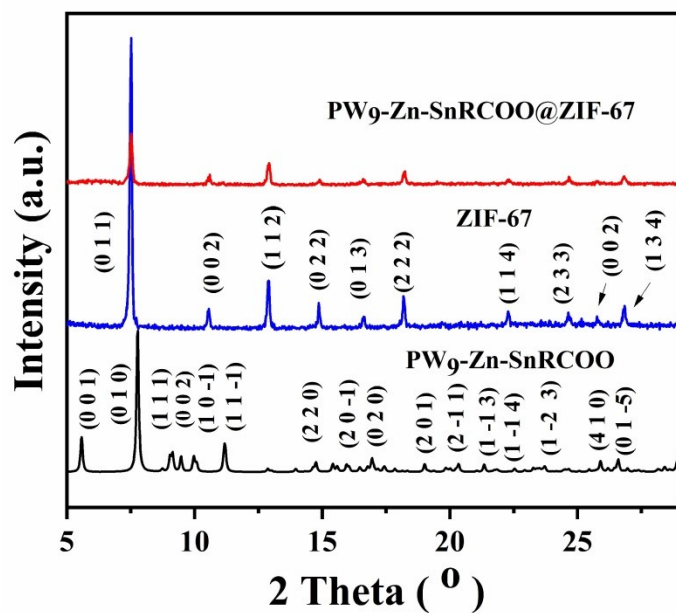


Fig. S2 PXRD patterns of $\text{PW}_9\text{-Zn-SnRCOO}$, ZIF-67 and $\text{PW}_9\text{-Zn-SnRCOO@ZIF-67}$.

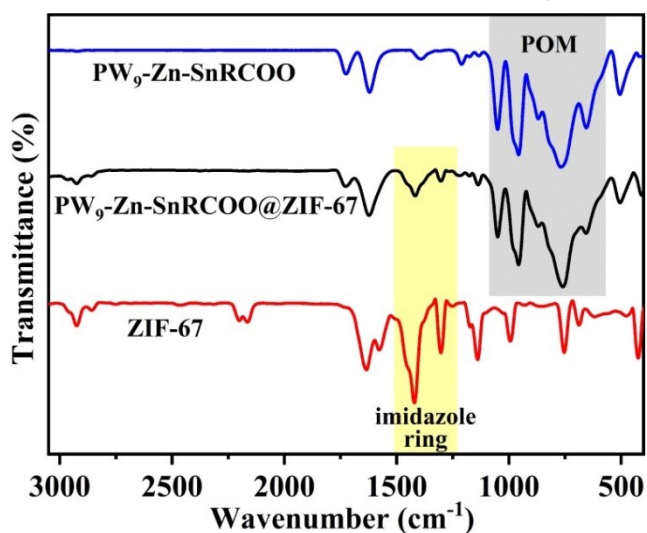


Fig. S3 IR spectra of $\text{PW}_9\text{-Zn-SnRCOO}$, ZIF-67, and $\text{PW}_9\text{-Zn-SnRCOO@ZIF-67}$.

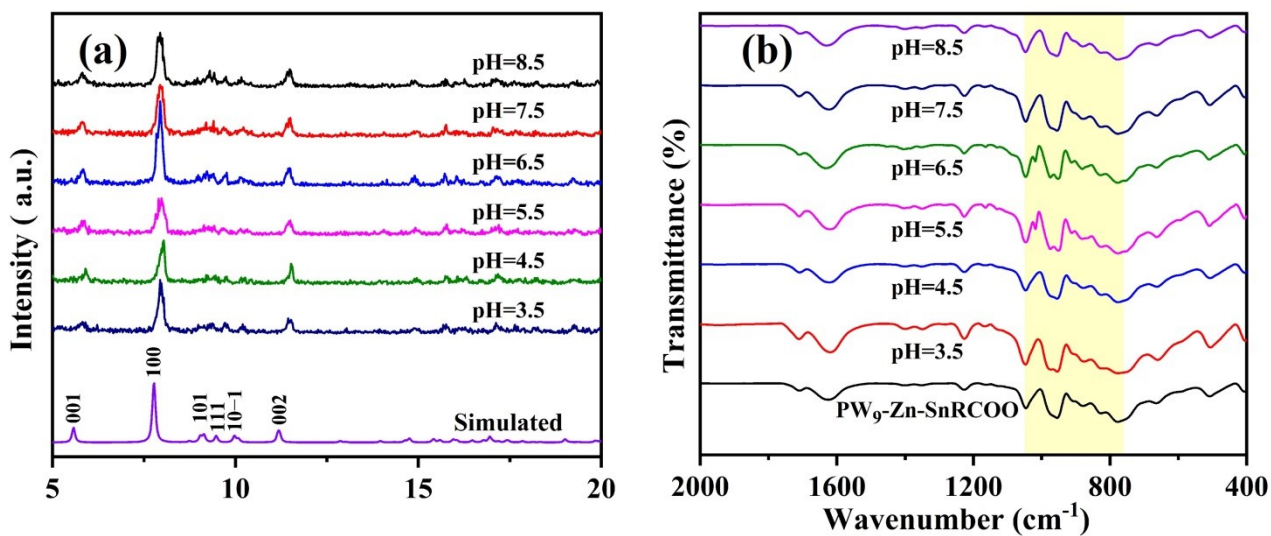


Fig. S4 (a) The PXRD and (b) IR plots of recrystallized samples for $\text{PW}_9\text{-Zn-SnRCOO}$ dissolved in different pH

solutions (3.5–8.5) for 5.0 h.

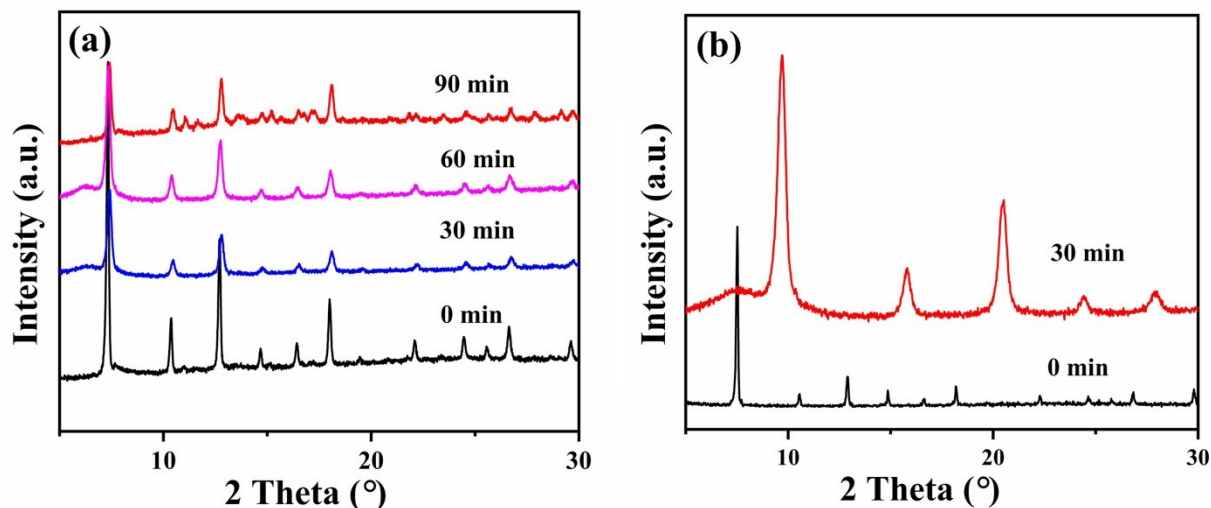


Fig. S5 (a, b) The PXRD patterns of PW₉-Zn-SnRCOO@ZIF-67 and ZIF-67 after soaked in a solution with pH 3.5 for 0–90 and 0–30 min, respectively.

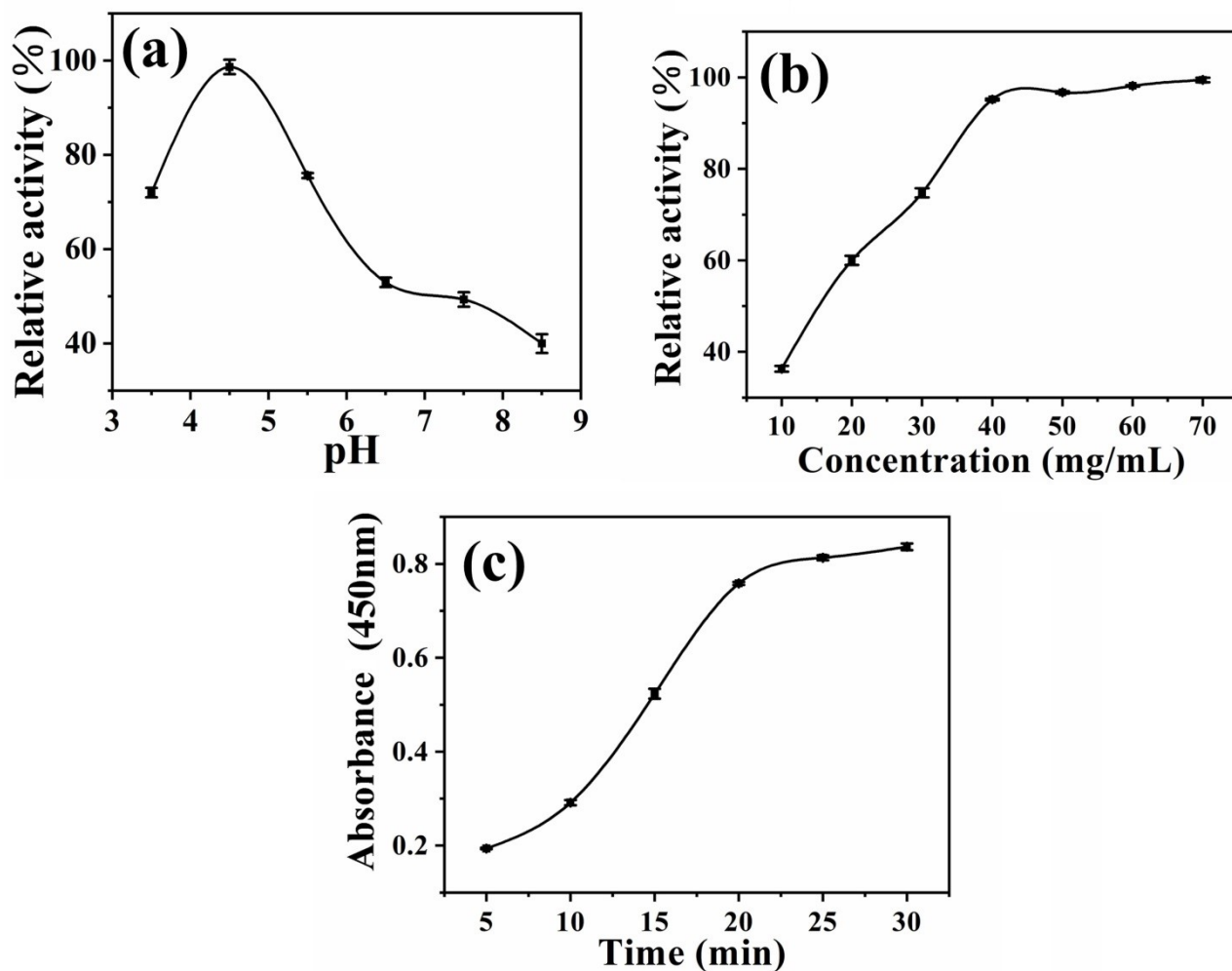


Fig. S6 (a–c) The effects of pH (3.5–8.5), PW₉-Zn-SnRCOO concentration (10.0–70.0 mg/mL) and reaction time (5–30 min) on the activity of PW₉-Zn-SnRCOO (Note: The reaction is carried out at room temperature, the error bars show the results of five parallel determinations; 30 μ L of POM, 40 μ L of 10.0 mM OPD, 100 μ L of 50.0 mM H₂O₂).

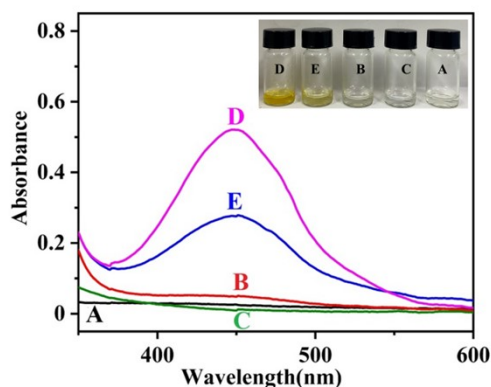


Fig. S7 The absorption spectra of different colorimetric reaction systems. Curves A–E represent the following substances: (A) OPD; (B) OPD+H₂O₂; (C) OPD+PW₉-Zn-SnRCOO; (D) OPD+PW₉-Zn-SnRCOO+H₂O₂ and (E) OPD+PW₉-Zn+H₂O₂. The PBS with pH 4.5 is used as the solvent.

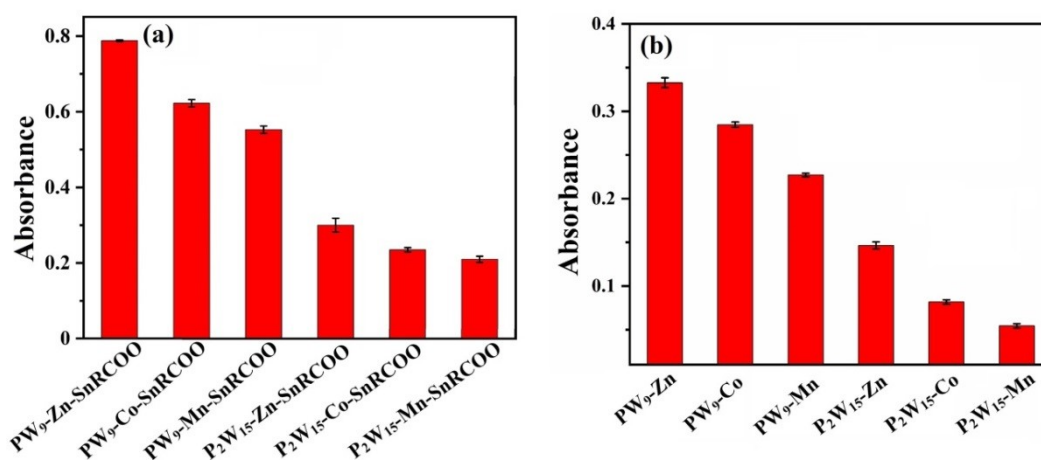


Fig. S8 The mimic peroxidase performance of PW₉-TM-SnRCOO and P₂W₁₅-TM-SnRCOO (a), and their parent compounds PW₉-TM and P₂W₁₅-TM (b) under the same reaction conditions: 40 μ L of 10.0 mM OPD, 100 μ L of 50.0 mM H₂O₂ and 30 μ L of 40.0 mg/mL POM; pH 4.5; 20 min, room temperature.

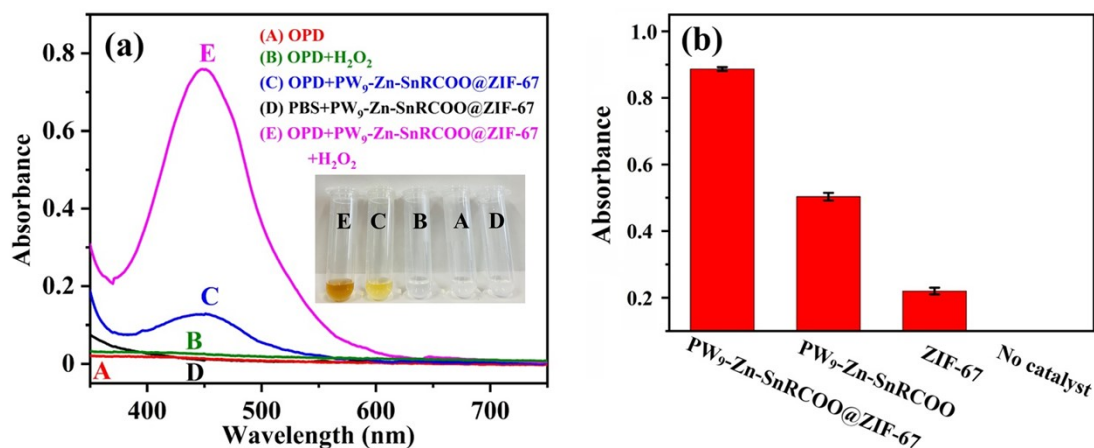


Fig. S9 (a) The absorption spectra of different colorimetric reaction systems. Reaction conditions: 30 μ L suspension of PW₉-Zn-SnRCOO@ZIF-67 (15.0 mg/mL), 40 μ L of 10.0 mM OPD, 100 μ L of 50.0 mM H₂O₂, and 330 μ L of PBS, pH 4.5. (b) Comparison of the catalytic activities of PW₉-Zn-SnRCOO, ZIF-67, and PW₉-Zn-SnRCOO@ZIF-67, the reactants added is the same as before. The total operation time for all experiments is 10 min.

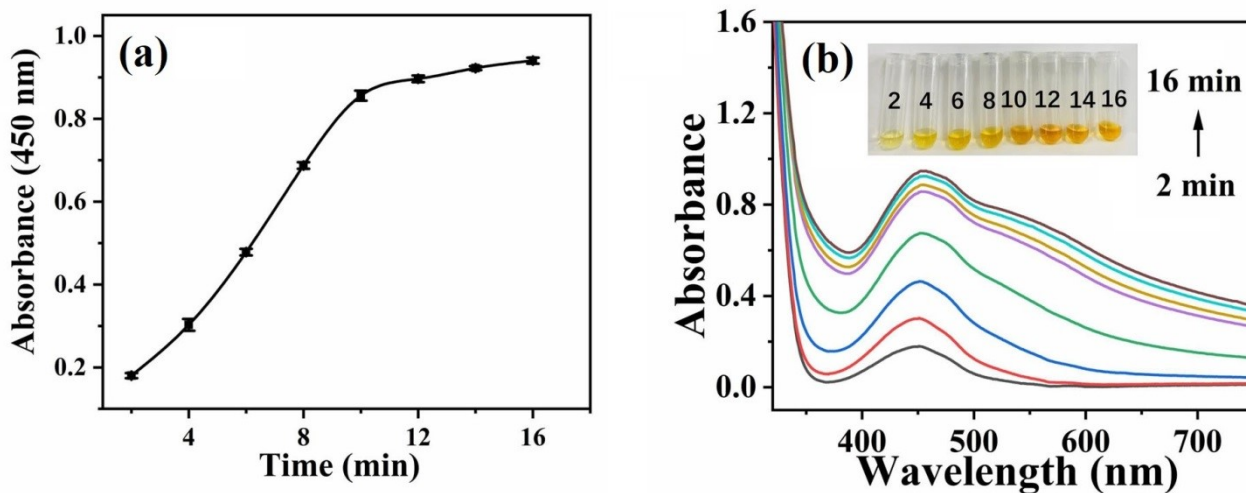


Fig. S10 (a) The relationship between the absorbance (λ_{450}) and the reaction time for the OPD reaction solution catalyzed by $\text{PW}_9\text{-Zn-SnRCOO@ZIF-67}$ (Note: The error bars show the results of 5 parallel determinations; pH 4.5, POM dosage 30.0 mg, other reaction conditions are the same as above); (b) The UV-Vis spectra of corresponding to figure (a).

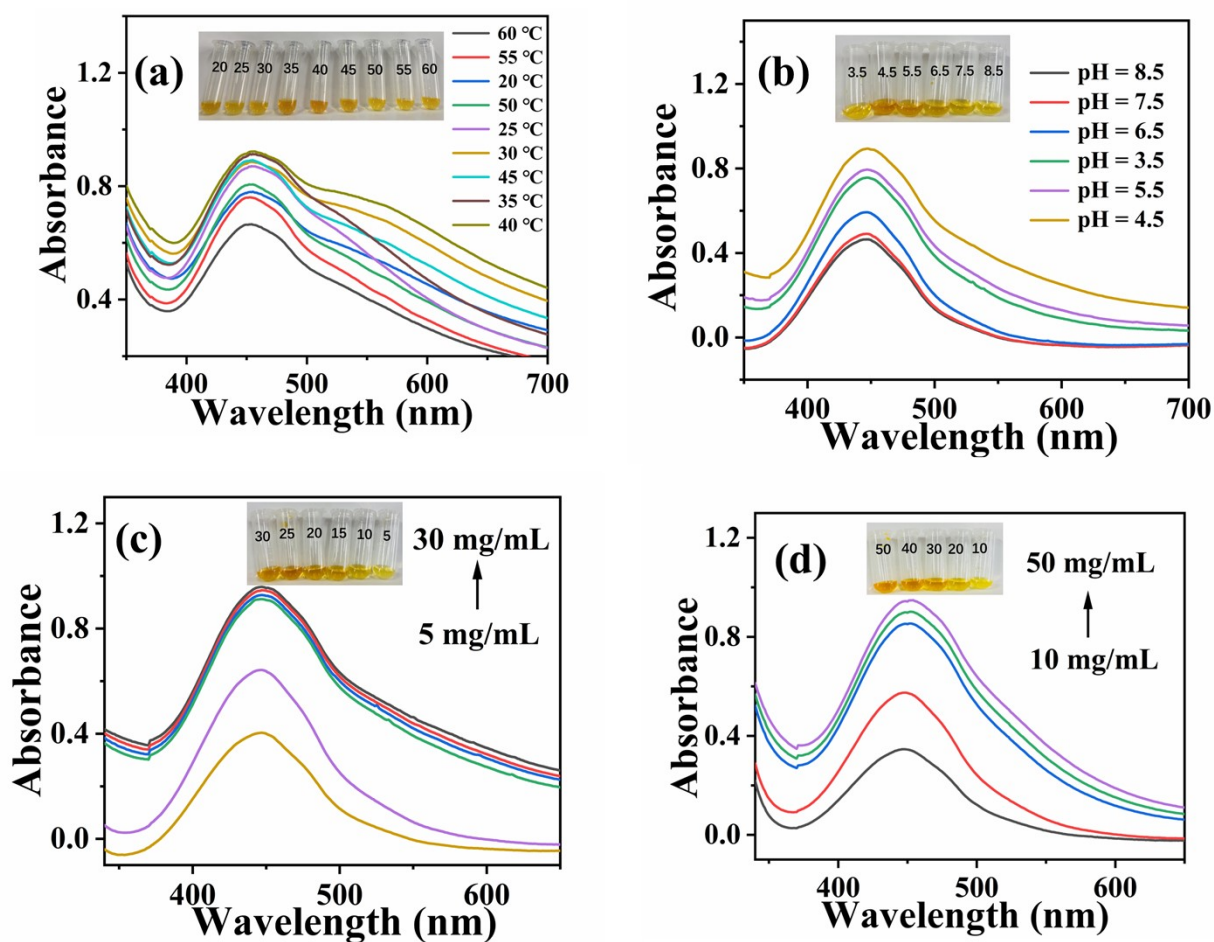


Fig. S11 UV-Vis absorption patterns of OPD reaction solution in the presence of $\text{PW}_9\text{-Zn-SnRCOO@ZIF-67}$ under different conditions: (a) reaction temperature; (b) pH; (c) the amount of composite materials used; (d) the amount of $\text{PW}_9\text{-Zn-SnRCOO}$ added.

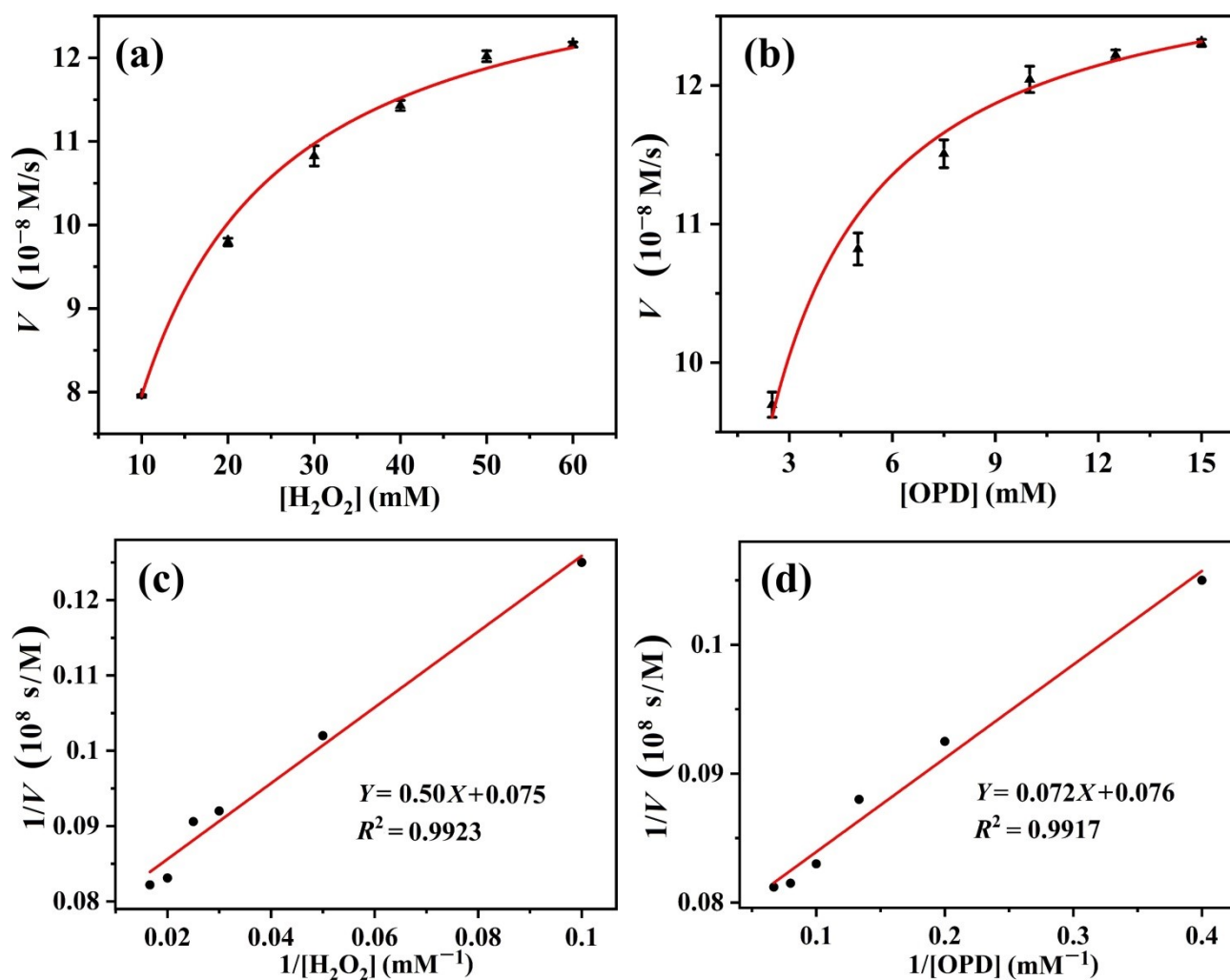


Fig. S12 The steady-state kinetics of the OPD oxidation catalyzed by $\text{PW}_9\text{-Zn-SnRCOO@ZIF-67}$. (a, c) the concentration of OPD was fixed at 10.0 mM, changing the concentration of H_2O_2 ; (b, d) the fixed concentration of H_2O_2 was 50.0 mM, changing the concentration of OPD. Other reaction conditions were unchanged.

Table S2 Comparison of the detection performance of different colorimetric sensors for acetone

Catalysts	Linear range (mM)	Detection limit (mM)	Refs.
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.05–3.0	0.035	11
Metal-organic framework	0.00–8.62	0.22	12
WS_2 nanosheets	0.17–2.15	0.05	62
$\text{PW}_9\text{-Zn-SnRCOO@ZIF-67}$	0.01–4.0	0.0074	This work

The mechanism of acetone detection

A. The trapping experiment of hydroxyl radicals

In order to investigate the possible principle for detecting acetone by colorimetric method during the mimetic HRP-catalyzed oxidation of OPD to DAP, according to the reported methods,⁶² we have prepared four samples (Samples 1–4), and then to conduct the fluorescence assay to monitor hydroxyl radicals ($\cdot\text{OH}$) concentration by terephthalic acid (TA) (Fig. S13†). TA can combine with $\cdot\text{OH}$ radicals and generate 2-HTA, exhibiting a strong blue fluorescence with peak at λ_{max} 440 (Fig. S13†). The specific operations were as follows:

(1) To a 30 μL of 15 mg/mL of suspension of **PW₉-Zn-SnRCOO@ZIF-67**, 20 μL of TA (0.5 mM) and 100 μL H_2O_2 (10.0 mM) were added successively, and the reaction mixture (Sample 1) was obtained, and then the fluorescence spectrum (curve I) was tested in Fig. S13. 0.1 M PBS (4.5) as a solvent, and the total volume are 500 μL .

(2) The amount of each component in Sample 2 is the same as that in Sample 1 except for acetone. After 50.0 μL acetone (4.0 mM) was added on this basis, the fluorescence spectrum of Sample 2 (curve II) was tested and illustrated in Fig. S13.

(3) To investigate whether H_2O_2 generates $\cdot\text{OH}$ in the absence of catalyst **PW₉-Zn-SnRCOO@ZIF-67**, 100 μL H_2O_2 (50.0 mM) was added to the PBS, obtaining Sample 3. The fluorescence spectrum intensity was relatively low, indicating the production of a small amount of $\cdot\text{OH}$ free radicals (curve III, Fig. S13). This proved that $\cdot\text{OH}$ free radicals play an important role during the enzyme-catalyzed H_2O_2 oxidation.

(4) For Sample 4, it has the same composition as sample 1, without adding TA, i. e., **PW₉-Zn-SnRCOO@ZIF-67** + PBS + H_2O_2 .

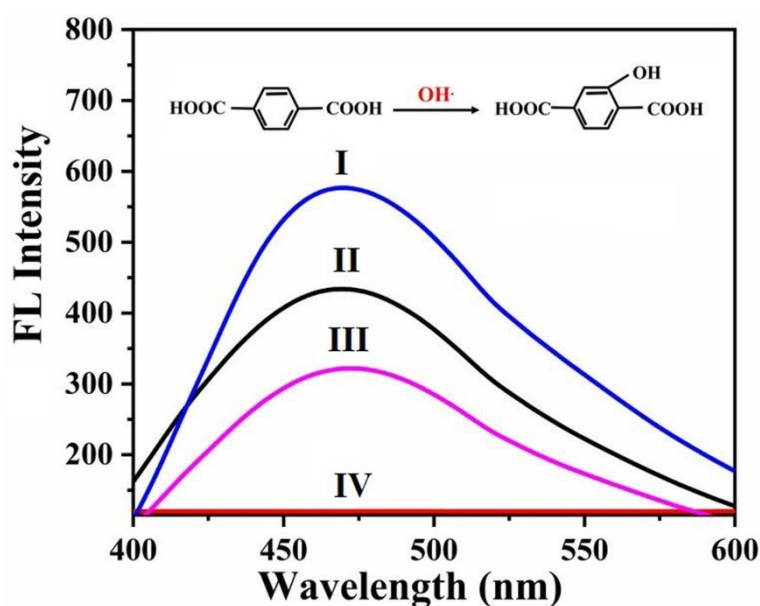


Fig. S13 Fluorescence spectra of the solutions containing different substances. Curves I–IV correspond to samples 1–4. Sample 1: **PW₉-Zn-SnRCOO@ZIF-67** + PBS + H_2O_2 + TA; Sample 2: Sample 1 + acetone; Sample 3: PBS + H_2O_2 + TA; Sample 4: **PW₉-Zn-SnRCOO@ZIF-67** + PBS + H_2O_2 .

B. The analysis of 1:1 complex of OPD and acetone

It was reported that when acetone is added to the reaction system simulating enzyme-catalyzed oxidation of OPD to generate DAP, a molar ratio of 1:1 complex of DAP and acetone would be formed.¹¹ To investigate whether the OPD oxidation catalyzed by **PW₉-Zn-SnRCOO@ZIF-67** reaction process also underwent the same mechanism of acetone inhibition, we tested the changes in absorbance of the yellow DAP solution before and after adding acetone. The specific operations were as follows:

(1) In the mixture containing 30 μL of 15 mg/mL of suspension of **PW₉-Zn-SnRCOO@ZIF-67** and 40 μL of 10.0 mM OPD, 100 μL of 50.0 mM H_2O_2 was added, and after reaction for 10 min at 40 °C, excessive isopropanol (50.0 mM) was added into the above reaction mixture to consume all $\cdot\text{OH}$ free radicals, and reacted for another 10 min, the absorbance of the yellow DAP solution was tested (Sample 1 in Fig. S14).

(2) When the absorbance values of the solution no longer change, adding acetone to the above reaction mixture and reacted for another 10 min, then measure the absorbance of the solution again (Sample 2 in Fig. S14).

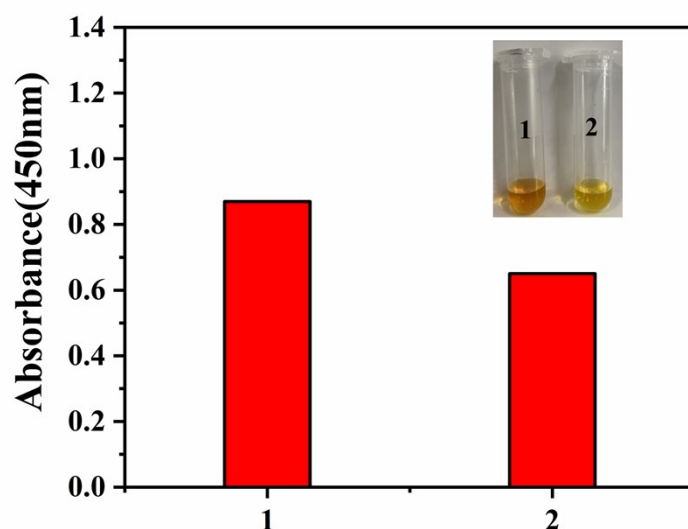


Fig. S14 Changes in absorbance of the yellow DAP solution before and after adding acetone. Sample 1: **PW₉-Zn-SnRCOO@ZIF-67** + PBS + H_2O_2 + OPD + isopropanol; Sample 2: sample 1 + acetone). The total reaction time was 30 min, and the reaction temperature was 40 °C.