Supporting Information

Investigation of the mimic enzyme activity of Two-dimensional Pd-based nanostructures

Jingping Wei, Xiaolan Chen, Saige Shi, Shiguang Mo and Nanfeng Zheng**

State Key Laboratory for Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, and Engineering Research Center for Nano-Preparation Technology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.
E-mail: chenxl@xmu.edu.cn; nfzheng@xmu.edu.cn.

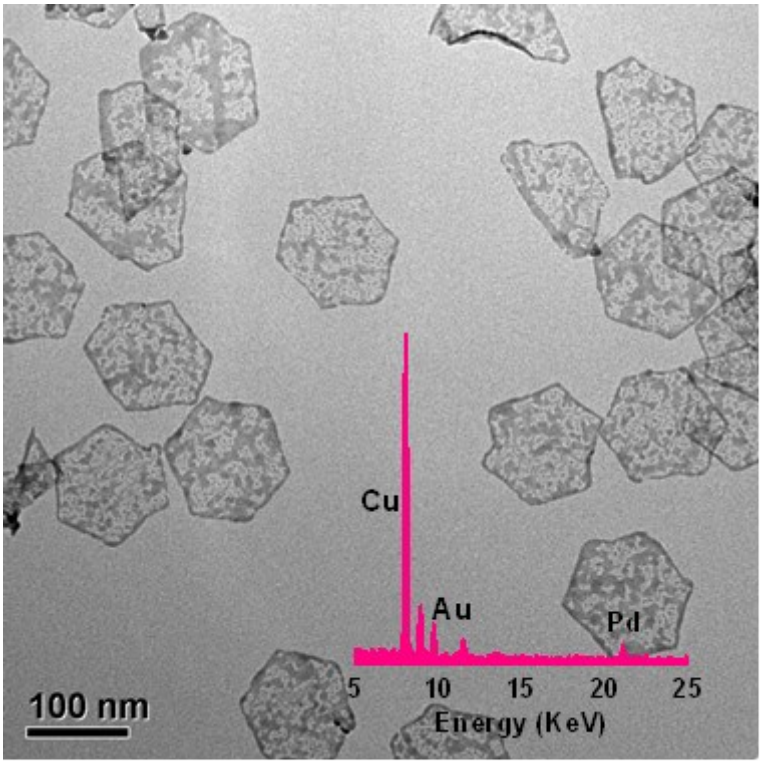


Fig.S1 TEM image and EDX of Pd@Au nanoplates.

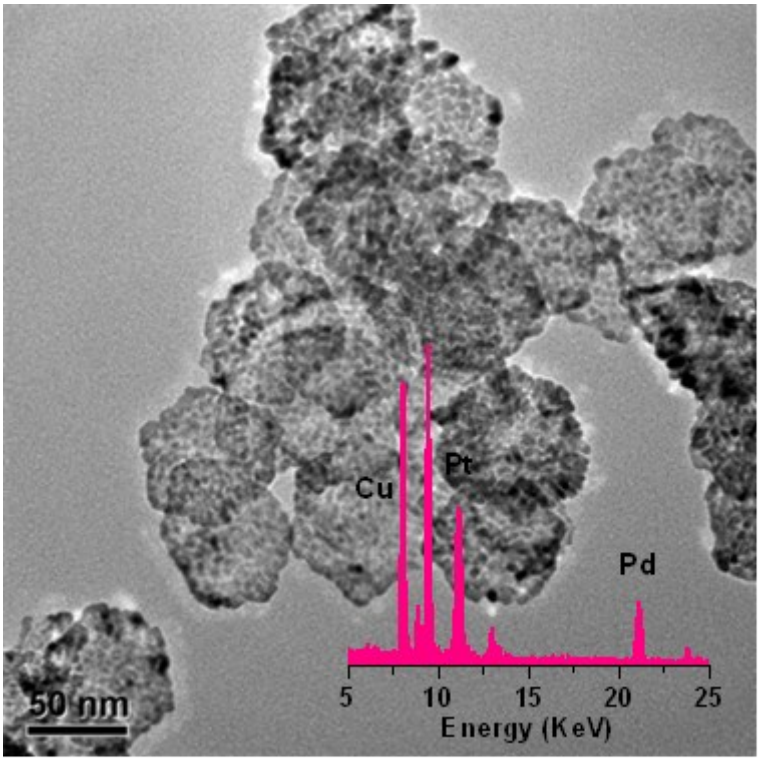


Fig.S2 TEM image and EDX of Pd@Pt nanoplates.

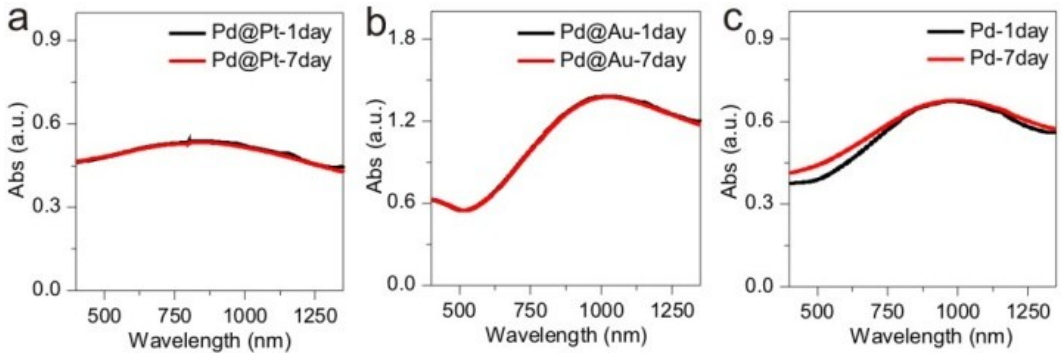


Fig.S3 Absorption spectra of 2D Pd-based nanomaterials dispersed in water for 1 day and 7 days. (a) Pd@Pt, (b) Pd@Au, and (c) Pd.

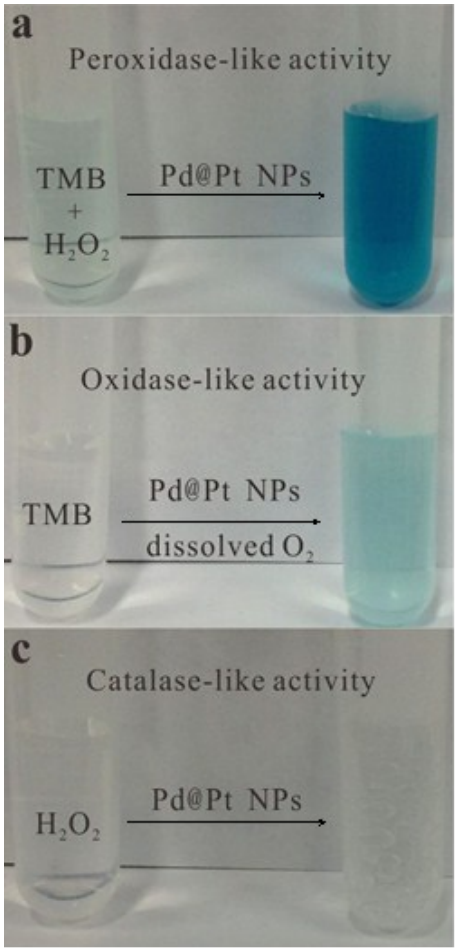
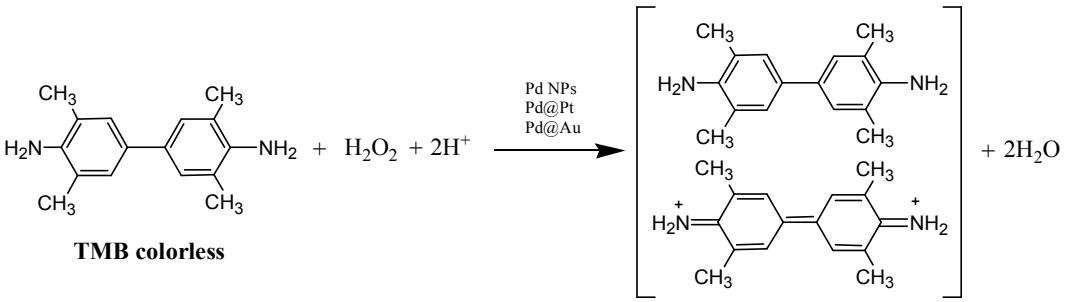


Fig.S4 Mimic enzymatic activity of 2D Pd-based nanostructures. Images of color reaction of TMB with H_2O_2 (a) or dissolved O_2 (b) in the presence of Pd@Pt. (c) Images of Pd@Pt as catalase-like catalyst to decompose H_2O_2 for generating O_2 gas bubbles.



TMB colorless

ox TMB(blue)

Scheme S1. Reaction mechanism for TMB oxidation with H_2O_2 catalyzed by Pd-based nanoplates.

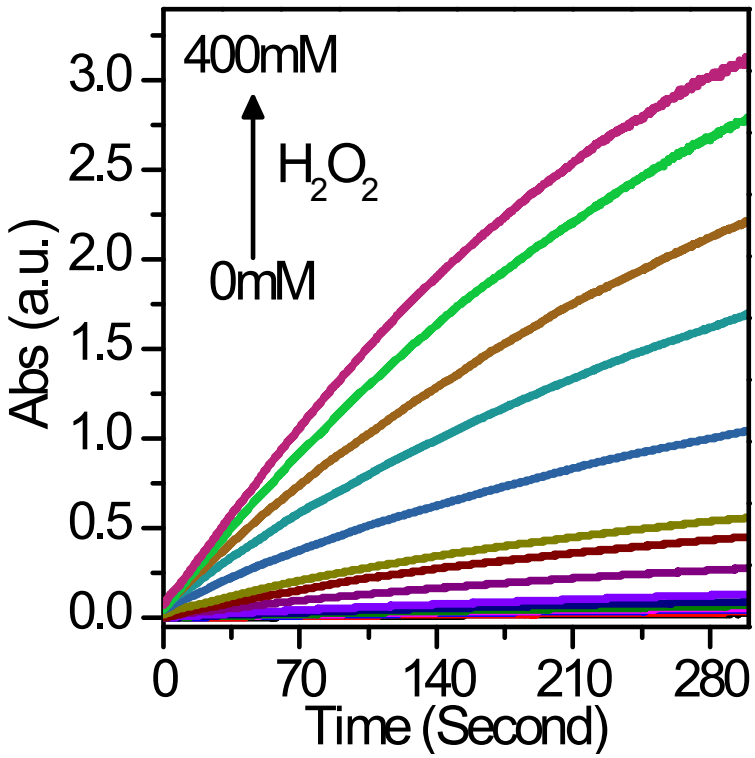


Fig.S5 Time-dependent absorbance changes at 652 nm with different H_2O_2 concentrations.

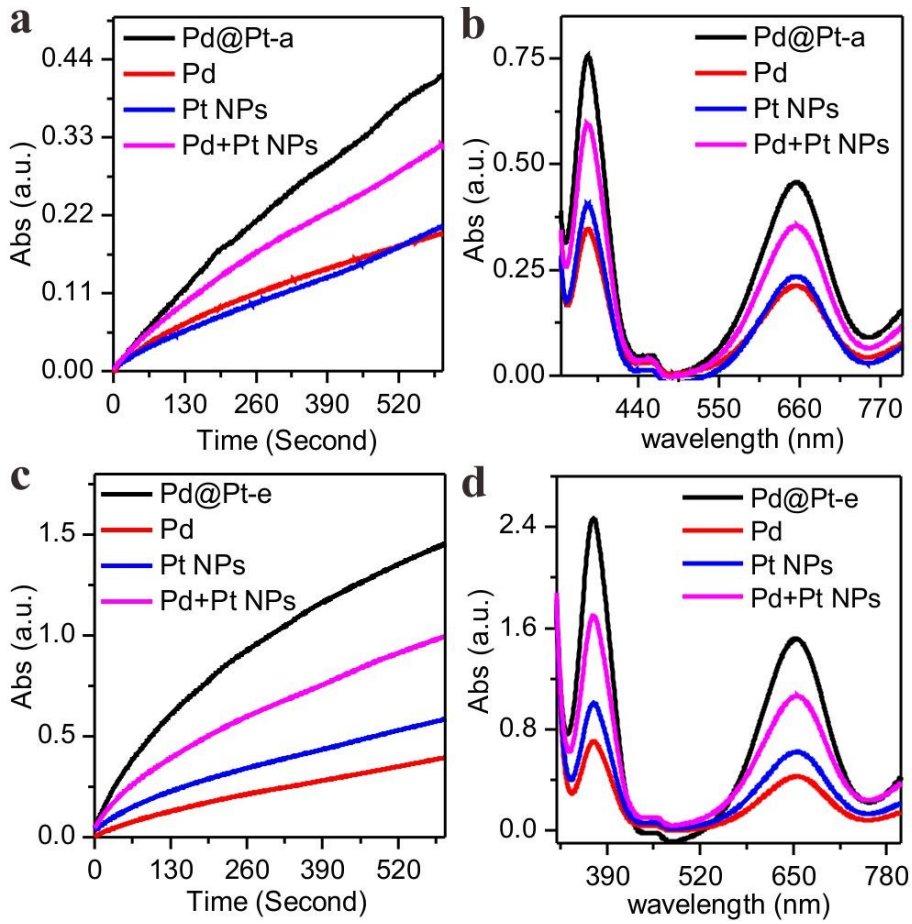


Fig.S6 The comparison of peroxidase activity of Pd@Pt-a (Pt/Pd=1.3) and Pd@Pt-e (Pt/Pd=12) with their corresponding monometallic components. Time-dependent absorbance changes at 652 nm (a and c) and UV-Vis spectra (b and d) of 0.5 mM TMB solutions containing 10 mM H_2O_2 with different catalysts: Pd@Pt, Pd, Pt NPs and physical mixture of Pd and Pt NPs (the amounts of Pd and Pt NPs are same as those in the Pd@Pt nanoplates).

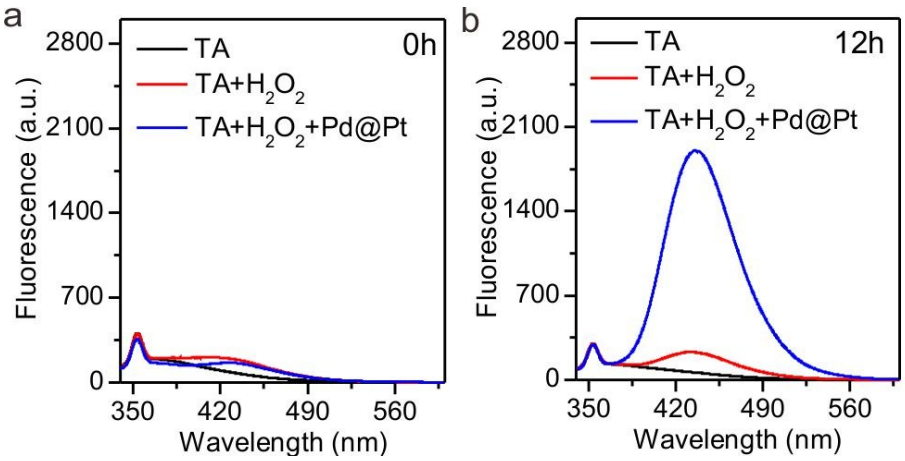


Fig.S7 Reaction between hydroxyl radical (•OH) and terephthalic acid (TA). Fluorescence spectra of the HAc-NaAc solutions include only TA, TA and H_2O_2, TA Pd@Pt and H_2O_2 before (Fig.S7a) and after 12 h reaction (Fig.S7b). The concentrations of TA, H_2O_2 and Pd@Pt were 0.5 mM, 10 mM and 2 μg, respectively.

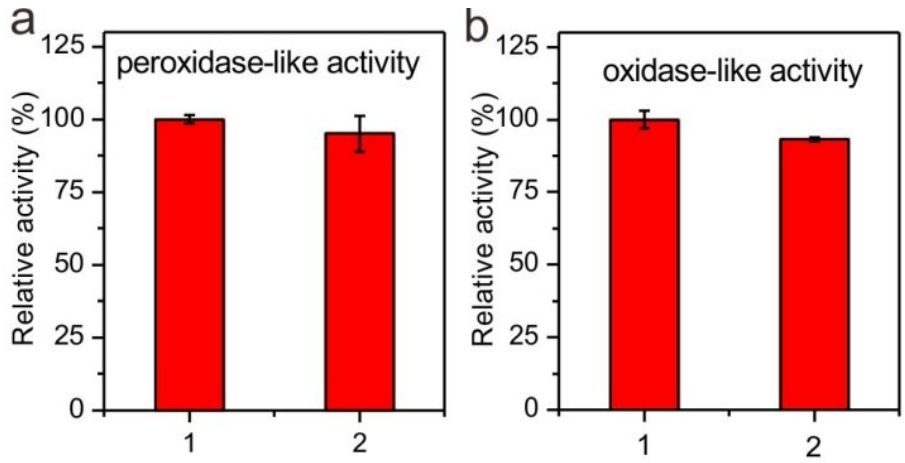


Fig.S8 Comparison of the peroxidase- (a) and oxidase- (b) like activities of Pd@Pt before (1) and after (2) centrifugation.

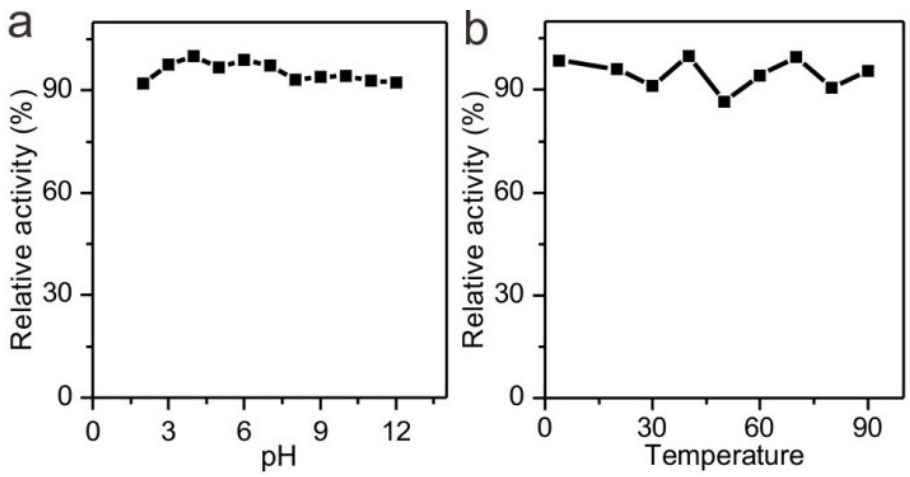


Fig.S9 Relative catalytic activity of the Pd@Pt nanoplates after incubation at a range of values of pH (2-12) (a) and a range of temperatures (4-90 °C) for 2 h (b).

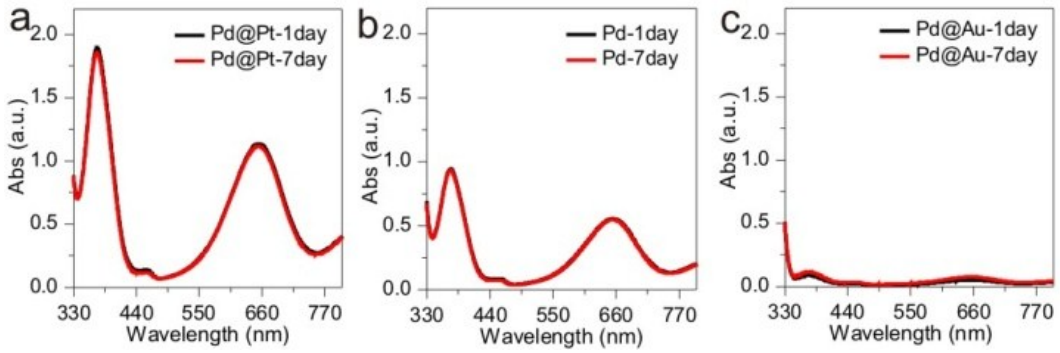


Fig.S10 UV-Vis absorption spectra of TMB oxidation by H_2O_2 in the presence of Pd-based nanomaterials with different storing time.

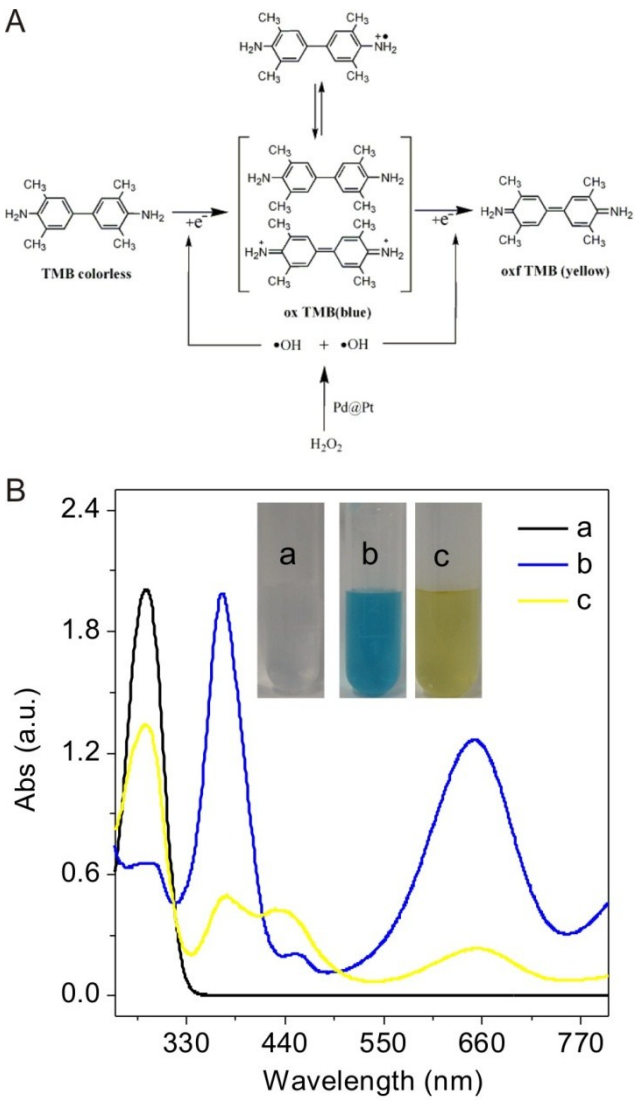


Fig.S11 (A) The catalytic oxidation mechanism of TMB. (B) The UV-Vis absorption spectra of TMB systems under different conditions. (a) TMB only, (b) TMB-H_2O_2-Pd@Pt with reaction for 10 min at room temperature, and (c) TMB-H_2O_2-Pd@Pt with reaction for 10 min at room temperature, then heating at 80 ℃ for 5 min.

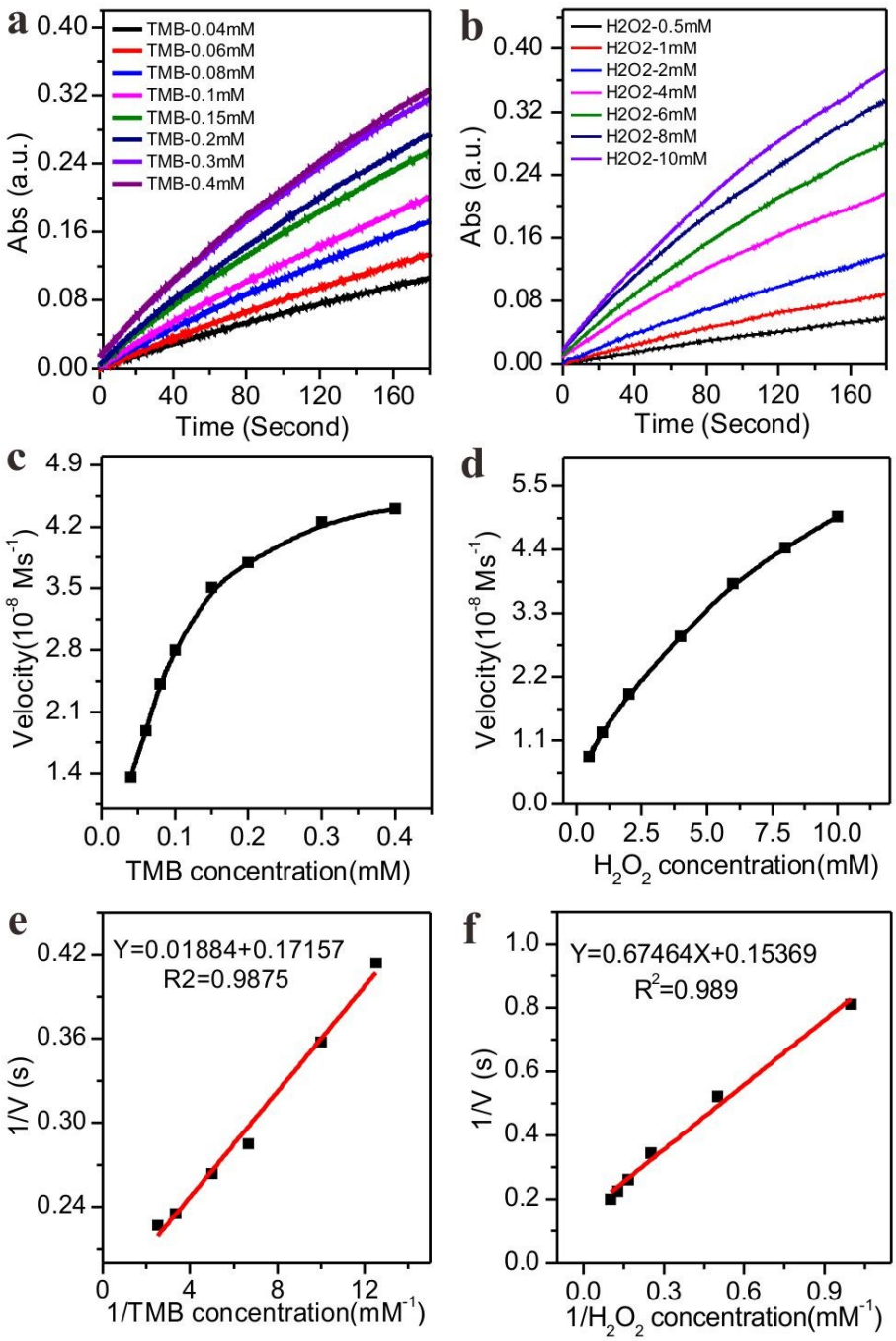


Fig.S12 Steady-state kinetic assay of Pd. Time-dependent absorbance changes at 652 nm of TMB reaction solutions catalyzed by the Pd in the presence of different concentrations of TMB (a) or H_2O_2 (b). The velocity (v) of the reaction changes in the presence of different concentrations of TMB (c) or H_2O_2 (d). Double reciprocal plot of Pd activity in the presence of different concentrations of TMB (e) or H_2O_2 (f), respectively. Experiments were carried out in acetic acid-sodium acetate buffer (pH 4.5) using 0.2 μg Pd at 25℃. (a), (c) and (e) H_2O_2 concentration was fixed at 10 mM and the TMB concentration was varied. (b), (d) and (f) TMB concentration was fixed at 0.5 mM and the H_2O_2 concentration was varied.

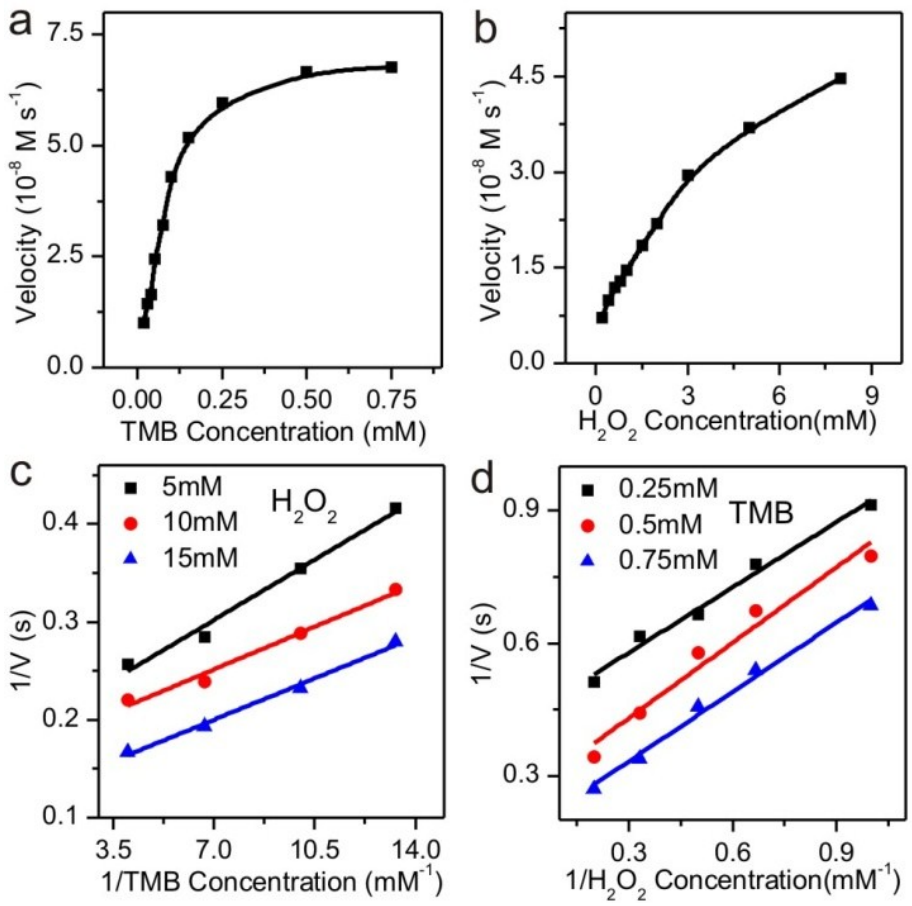


Fig.S13 Steady-state kinetic assay and catalytic mechanism of Pd@Pt. The velocity (v) of the reaction was measured using 0.2 μg mL^{-1} Pd@Pt in 2 mL of HAc-NaAc, pH 4.5. c and d, Double-reciprocal plots of activity of Pd@Pt at a fixed concentration of one substrate versus varying concentration of the second substrate for H_2O_2 and TMB.

Detailed calculating process for K_m and V_{max}

The detailed calculating process for the Michaelis–Menten constant K_m and the maximum initial velocity V_{max} is:

∵ A = εbc, ε=3.9*10^4 M^{-1}·cm^{-1}, b=1 cm (c: molar concentration)

∴ c=A/εb

∵ Reaction rate: V =Δc/Δt

∴ V =ΔA/εbΔt=k/εb (k=ΔA/Δt)

Then according to the relationship between the absorbance values (λ =652 nm) of different substrate concentrations and time (Fig. 5a and

5b), we fitted straight line and got its slope k ($k=\Delta A/\Delta t$). Therefore, the reaction initial rate of different substrate concentration can be obtained by $V= k/\varepsilon b$, and the unit of V is M s^{-1}. Finally, these data were fitted to the Lineweaver–Burk graphs (1/V versus 1/[S]) to get the Michaelis–Menten constant Km and the maximum initial velocity Vmax.

Experimental condition optimization

The catalytic activity of the Pd-based nanoplates is dependent on pH,temperature, the concentration of catalyst, and H_2O_2 concentration. In the work, Pd@Pt nanoplates were chosen as the model catalysts to study the catalytic activity in different experimental conditions.

The peroxidase-like activity of Pd@Pt nanoplates at different temperature: A series of 2 mL acetic acid-sodium acetate buffer solution (pH=4.5) containing 0.5 mM TMB, 10 mM H_2O_2 and Pd@Pt nanoplates (0.2μg) were reacted at different temperature for 5 min, then the UV-Vis absorption spectra of the solutions were measured. Peroxidase-like activity of Pd@Pt nanoplates at different temperature was obtained by comparing their absorption intensity at 652nm (The maximum point in the curve was set as 100%).

The peroxidase-like activity of Pd@Pt nanoplates in different pH: Pd@Pt nanoplates (2 μg) was added respectively in 2mL acetic acid-

sodium acetate buffer solution with different pH (2.0, 3.3, 4.2, 4.5, 4.9, 5.5, 6.1, 7.2, 8.2, 9.5 and 11.3) containing 0.25mM TMB and 1mM H_2O_2.The UV-Vis absorption spectra of the solutions were measured after reacting for 3 min at room temperature. Peroxidase-like activity of Pd@Pt nanoplatesin different pH was obtained by comparing their absorption intensity at 652nm (The maximum point in the curve was set as 100%).

The peroxidase-like activity of Pd@Pt nanoplates with different concentrations: To a series of 2 mL acetic acid-sodium acetate buffer solutions containing same concentrations of H_2O_2 (10mM) and TMB (0.5mM), Pd@Pt catalysts with different amounts (0-0.65 μg) were added, respectively. The absorbance change at 652 nm in 5min was measured on a UV-Vis spectrophotometer.

The peroxidase-like activity of Pd@Pt nanoplates in different H_2O_2 concentrations: The experimental process is similar to that mentioned above. While keeping the concentrations of catalyst (0.2μg) and TMB (0.5mM) unchanged, the concentrations of H_2O_2 were changed to obtain the time-dependent absorbance changes at 652 nm.