Electronic Supplementary Information

Aqueous synthesis of porous platinum nanotubes at room temperature and their intrinsic peroxidase-like activity

Kai Cai, Zhicheng Lv, Kun Chen, Liang Huang, Jing Wang, Feng Shao, Yanjun Wang and Heyou Han*

State Key Laboratory of Agricultural Microbiology, College of Science, Huazhong Agricultural University, Wuhan 430070, China. Fax: +86-27-87288246; Tel.: +86-27-87288246; E-mail: hyhan@mail.hzau.edu.cn

Experimental Section

Materials: Tellurium dioxide powder (TeO_2, 99.99%) was purchased from Aladdin Chemistry Co., Ltd. Hexadecyltrimethylammonium bromide (CTAB, 99%), 3,3',5,5'-tetramethylbenzidine (TMB, 99%) and sodium dodecyl sulfate (SDS, 99%) were purchased from Sigma-Aldrich. Hydrazine monohydrate (85%, AR), hydrogen peroxide (H_2O_2, 30%, AR), chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, AR), and sodium hydrate (NaOH, AR) were supplied by Sinopharm Chemical Reagent Co., Ltd. Ultrapure water with a conductivity of 18.25 MΩ cm was used throughout the experiments, and all chemicals were used without further purification.

Apparatus: Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were made on a JEM-2010FEF high-resolution transmission electron microscopy at an accelerating voltage of 200 kV. The energy-dispersive X-ray spectroscopy (EDS) analysis was also done using a JEM-2010FEF transmission electron microscope with an EDAX attachment operating at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) analysis was carried out on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on Nicolet Evolution 300 Ultraviolet-Visible spectrometer.

Preparation of Te nanowires (TeNWs): TeNWs were prepared according to the method reported by Chang *et al.*[1] Typically, Hydrazine monohydrate (5 mL) was added slowly to a beaker containing tellurium dioxide (0.032 g) at room temperature under constant magnetic stirring. The solution changed color from colorless to blue after 60 min, indicating the formation of TeNWs (average length: 220 nm; average diameter: 15 nm). To terminate the reaction and stabilize the TeNWs, the mixture was diluted 10-fold with SDS (10 mM), which was then subjected to a centrifugation/wash cycle to remove most of the matrices, including SDS and hydrazine.

Synthesis of porous Pt nanotubes (PtNTs): In a typical synthesis, TeNWs (~0.01 mmol) from the previous experiment were dispersed in 10mL of CTAB solution (1 mM) under constant magnetic stirring. After 15 min, 0.1 M NaOH was added to the H_2PtCl_6 (~0.002 mmol) to adjust the pH to 7.0, and then the mixture was added to the solvent containing TeNWs. The solution changed color from blue to grey black after 50 min, indicating the formation of Te@Pt core-shell nanostructure. The mixture was subjected to a centrifugation/wash cycle to remove most of the matrices, including CTAB. Then the flocculation, that was the intermediate products, was re-dispersed in water (0.5 mL) and maintained at room temperature for 3 h. After a centrifugation/wash cycle, porous PtNTs were obtained.

Kinetic analysis: Kinetic measurements were carried out in time-drive mode by monitoring the absorbance change at 652 nm on a UV-Vis spectrophotometer. Experiments were carried out using 1.0 μg mL^{-1} PtNTs in a reaction volume of 2 mL buffer solution (100 mM citrate buffer solution, pH 4.0) with 0.13 mM TMB as substrate, and H_2O_2 concentration was 150 mM, unless otherwise stated. The Michaelis-Menten constant was calculated using Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equation, $1/v = (K_m/V_{max})\cdot(1/[S] + 1/K_m)$.

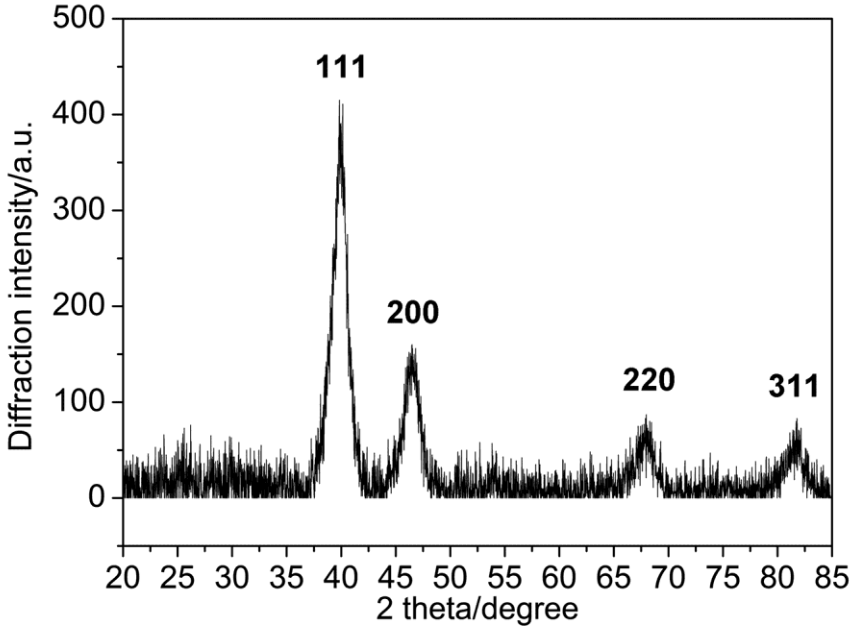

Fig. S1 XRD pattern of the porous Pt nanotubes.

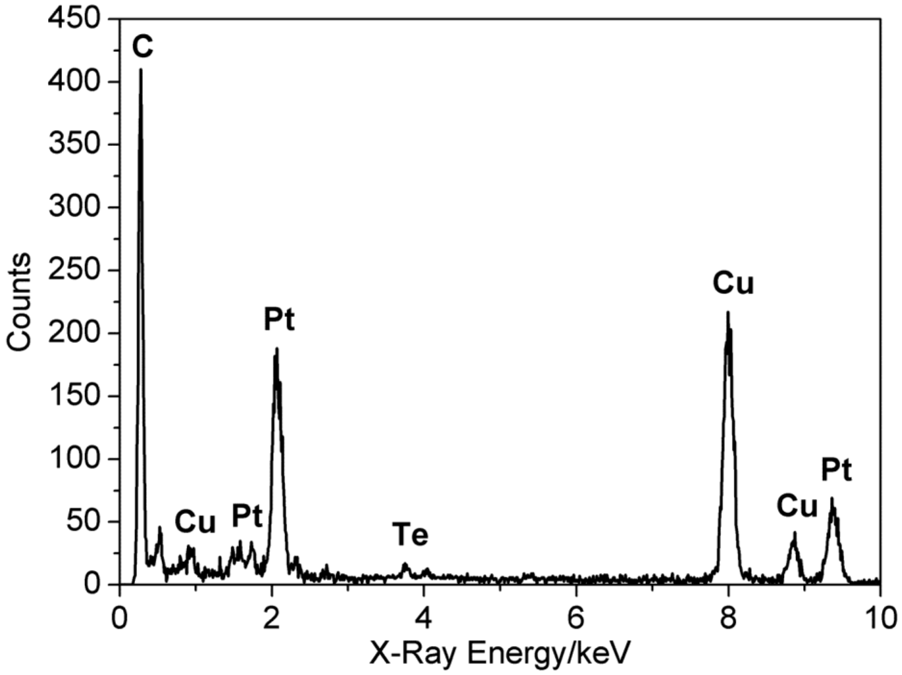

Fig. S2 EDS spectrum of the porous Pt nanotubes.

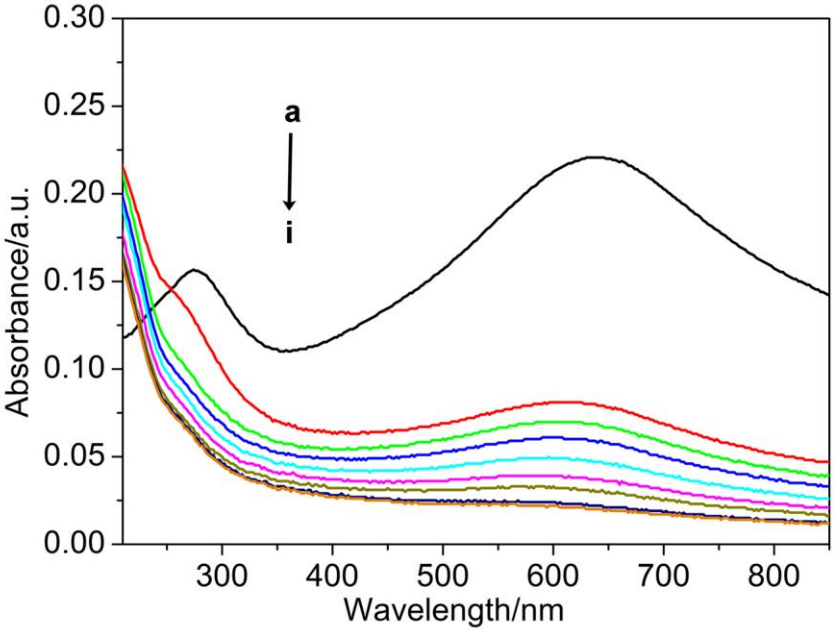

Fig. S3 UV-vis absorption spectra of the TeNWs and Te@Pt core-shell nanostructure. (a) TeNWs, (b) sample of the Te@Pt core-shell nanostructure after re-dispersing in aqueous solvent for 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 75 min, (g) 90 min, (h) 105 min, and (i) 120 min, respectively.

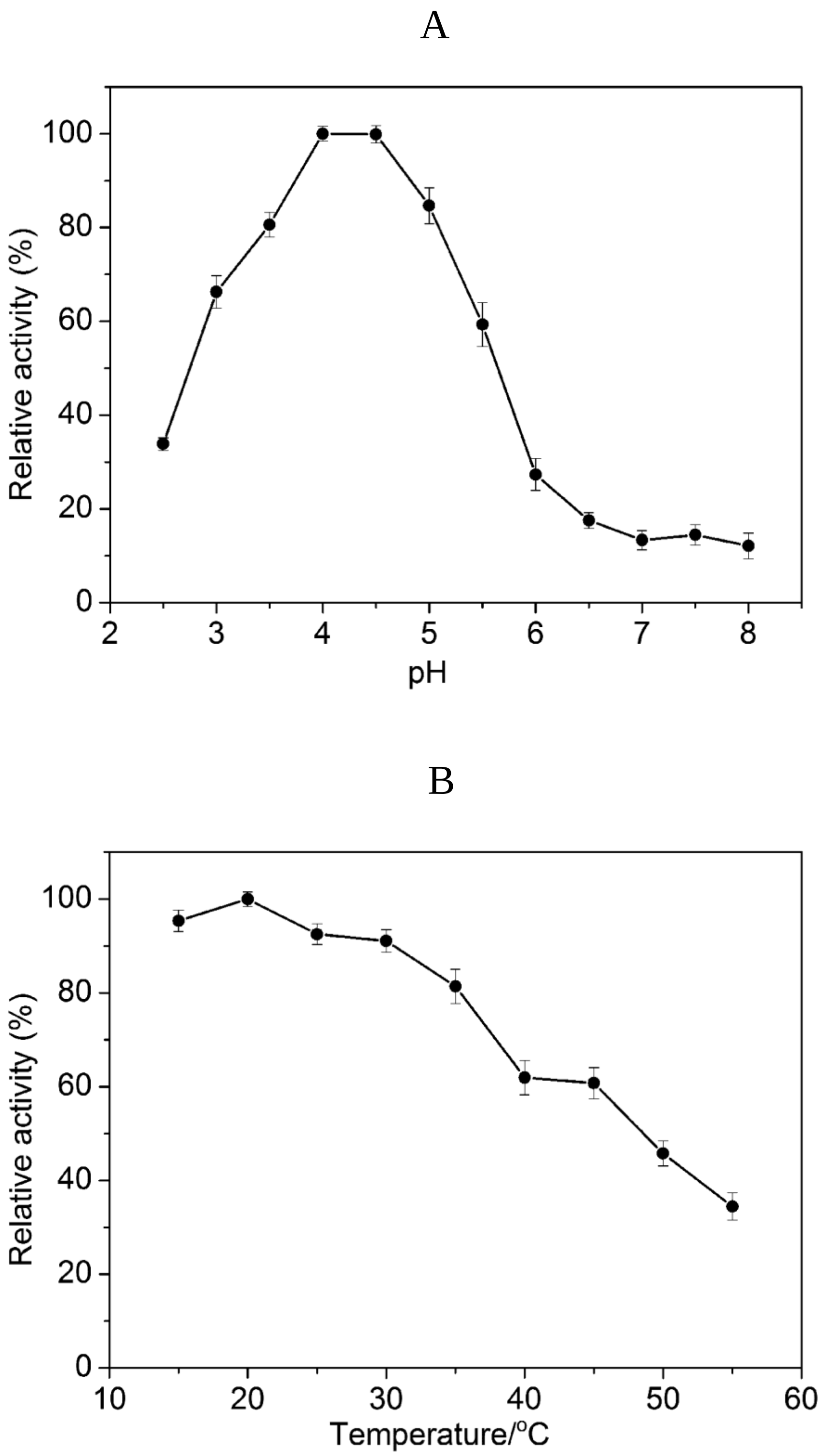

Fig. S4 Dependency of the PtNTs peroxidase-like activity on pH (A), and temperature (B). The error bars represent the standard deviation of three measurements. Experiments were carried out using 1.0 μg mL^{-1} PtNTs in citrate buffer solution with TMB (0.13 mM), H_2O_2 (150 mM), and 25 ^{o}C (A), pH 4.0 (B).

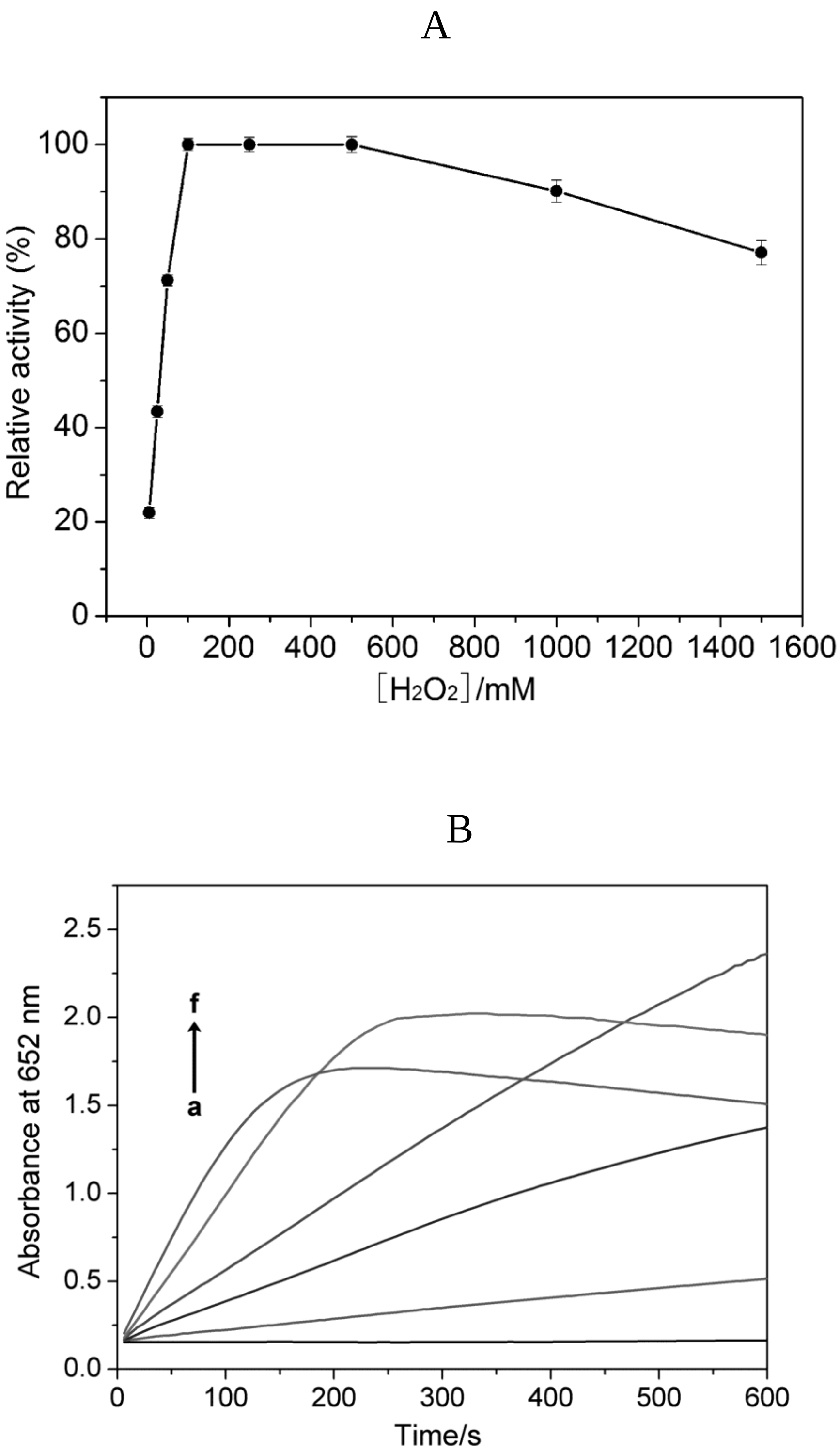

Fig. S5 (A) Dependency of the PtNTs peroxidase-like activity on H_2O_2 concentration. The error bars represent the standard deviation of three measurements. (B) The absorbance evolution at 652 nm over time at several H_2O_2 concentration: (a) 0 mM, (b) 5 mM, (c) 50 mM, (d) 150 mM, (e) 0.5 M, (f) 1.0 M.

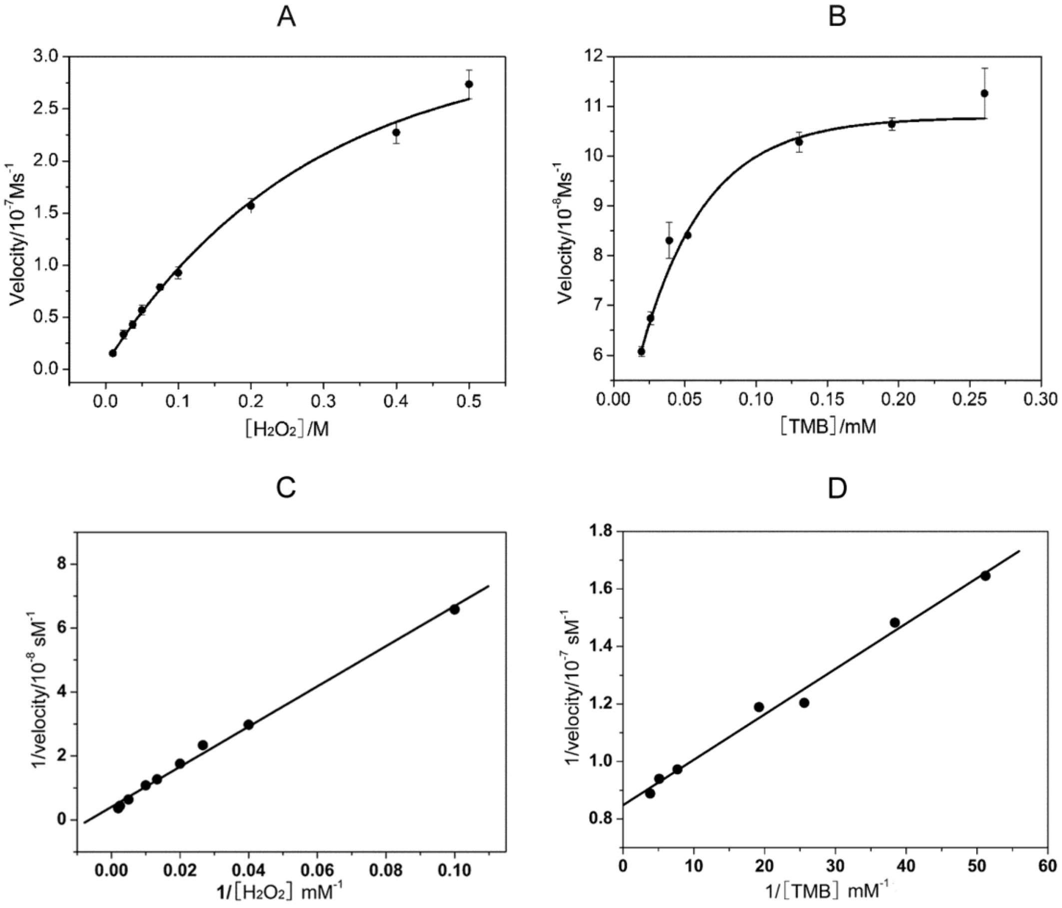

Fig. S6 Steady-state kinetic assay of PtNTs. The velocity of the reaction was measured using 1.0 μg mL^{-1} PtNTs in citrate buffer solution (pH 4.0) at 20 °C. The error bars represent the standard error derived from three repeated measurements. (A) The concentration of TMB was 0.13 mM and the H_2O_2 concentration was varied. (B) The concentration of H_2O_2 was 150 mM and the TMB concentration was varied. (C-D) Double-reciprocal plots of activity of PtNTs at a fixed concentration of one substrate versus varying concentration of the second substrate for H_2O_2 and TMB.

Table S1 Comparison of the kinetic parameters of different nanomaterials and HRP (H_2O_2 as a substrate). K_m is the michaelis constant, V_{max} is the maximal reaction rate.

	K_m[mM]	V_{max}[M s^{-1}]
HRP[2]	3.70	8.71×10^{-8}
GO-COOH[3]	3.99	3.85×10^{-8}
$ZnFe_2O_4$ MNPs[4]	1.66	7.74×10^{-8}
Fe_3O_4 MNPs[2]	154	9.78×10^{-8}
Co_3O_4 NPs[5]	140.07	12.1×10^{-8}
PtNTs	155	24.66×10^{-8}
C-Dots[6]	26.77	30.61×10^{-8}

References

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