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Supporting Information

Precisely modulated 2D PdCu alloy nanodendrites as highly active peroxidase mimics for the elimination of biofilms

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S1. Experiment section

S1.1 Materials

All chemicals were of analytical grade. Palladium (II) chloride ($PdCl_2$), copper (II) chloride ($CuCl_2$, 99%), 3,3,5,5-tetramethylbenzidine (TMB) and terephthalic acid (TA) were purchased from Sigma-Aldrich. Hydrogen chloride (HCl, 35-36%), and ascorbic acid (AA, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrafiltered water used in all the reactions was obtained by using a Millipore purification system. All chemicals were of analytical grade and used without further purification.

S1.2 Measurement of peroxidase-like activity and steady-state kinetic assays

The peroxidase-like activity of the PdCu nanostructure was measured using TMB as the substrate in the presence of H_2O_2. The PdCu nanostructures dispersions were diluted with NaAc buffer (0.2 M, pH = 3.6) as the substrate and then TMB solution (40 mM) and H_2O_2 (0.1 M) was added. The absorbance of the reaction solution at 652 nm was recorded at different times using a UV spectrometer (UV-3600, Shimadzu, Japan). For the assay of the product, •OH, a fluorescence probe TA (hydroxyterephthalic acid) was added into the reaction solution, and then the fluorescence spectra of the samples were collected using fluorescence spectroscopy (FLS980, Edinburgh). The steady-state kinetic assays were conducted at room temperature in a 200 μL NaAc buffer (0.2 M, pH = 3.6) with PdCu nanostructures (10 μg/mL) as catalysts in the presence of H_2O_2 and TMB. The kinetic assays of PdCu nanostructures with TMB as the substrate were performed by adding H_2O_2 (0.1 M) and different amounts of TMB solution. The kinetic assays of PdCu nanostructures with H_2O_2 as the substrate were performed by adding TMB (40 mM) and different amounts of H_2O_2 solution. All the reactions were monitored by measuring the absorbance at different reaction times. The apparent kinetic parameters were calculated based on the Michaelis–Menten equation (**Equation 1**):

$$V = V_{max} \times [S]/(K_m \times [S]) \quad (1)$$

V: initial reaction velocity, V_{max}: maximal reaction rate, [S]: substrate concentration, and K_m: Michaelis constant.

S1.3 Density function theory calculation

The Pd(111) surface was first built as a $p(5 \times 5)$ slab with a thickness of four Pd atom layers (dimension size: 13.76 Å × 13.76 Å × 5.84 Å), and 100 Pd atom was contained in the initial slab model. It has been shown that the $p(5 \times 5)$ slab is large enough to avoid the interactions between neighboring adsorbed H_2O_2 and to fully release the interfacial strain energy. To simulate the effects of the Pd/Cu ratio on the adsorption of H_2O_2, a series of surface models of PdCu alloy were created by substituting Pd atoms with Cu evenly. The number of the replaced Pd ranged from 8 to 13. The neighboring slabs were separated in the direction perpendicular to the surface by a vacuum region of 20 Å, and only the bottom atoms in the slab were frozen to their crystal lattice positions.

DFT calculations were performed using Dmol software with the conductor-like screening model (COSMO). The exchange-correlation potential was described by the revised Perdew-Burke-Ernzerhof (rPBE) generalized gradient approach (GGA), which improves the calculated adsorption energetics. The atomic orbitals were represented by a double numerical basis set plus polarization function (DNP). The SCF convergence criterion was set at 1.0×10^{-6} hartree/atom and the convergence criterion for structure optimization at 1.0×10^{-5} Hartree/bohr. Brillouin zone sampling was performed using a 4 × 4 × 1 k-point mesh. The adsorption energy is defined as **Equation 2**:

$$E_{ads} = E(\text{slab} + H_2O_2) - [E(\text{slab}) + E(H_2O_2)] \quad (2)$$

where $E(\text{slab} + H_2O_2)$ represents the energy of the optimized slab model with adsorbed H_2O_2; $E(\text{slab})$ and $E(H_2O_2)$ denote the energies of the separately optimized slab and H_2O_2, respectively.

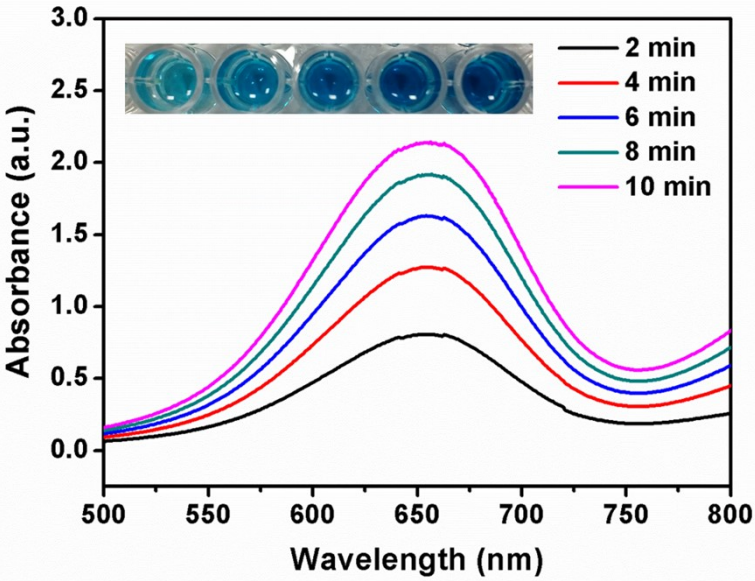

Fig. S1 UV-vis spectroscopy of samples containing 40 mM TMB, 0.1 M H_2O_2, and 10 μg/mL $Pd_{9.2}Cu$ NDs in 0.2 M acetate buffer (pH 3.6) for 10 min. The wells (inset) show the color change of TMB at different time points.

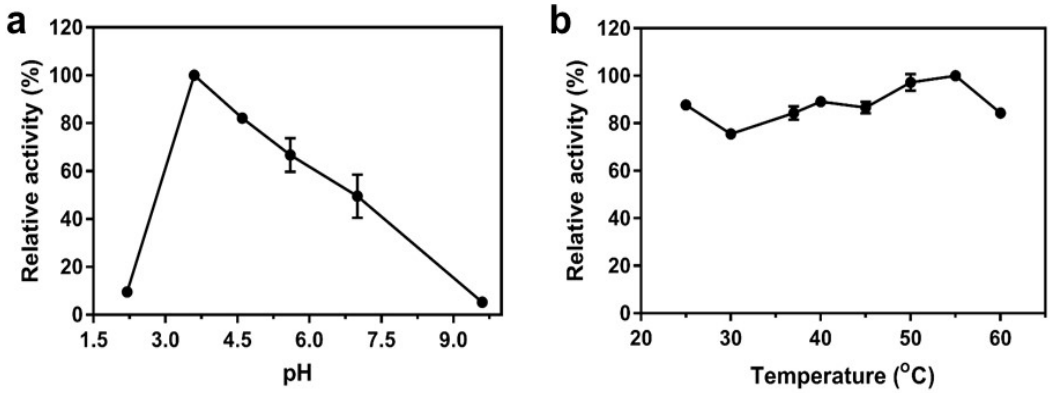

Fig. S2 Effects of (a) pH and (b) temperature on peroxidase-like activity of $Pd_{9.2}Cu$ NDs. [H_2O_2] = 0.1 M, [$Pd_{9.2}Cu$ NDs] = 10 μg/mL, [TMB] = 40 mM.

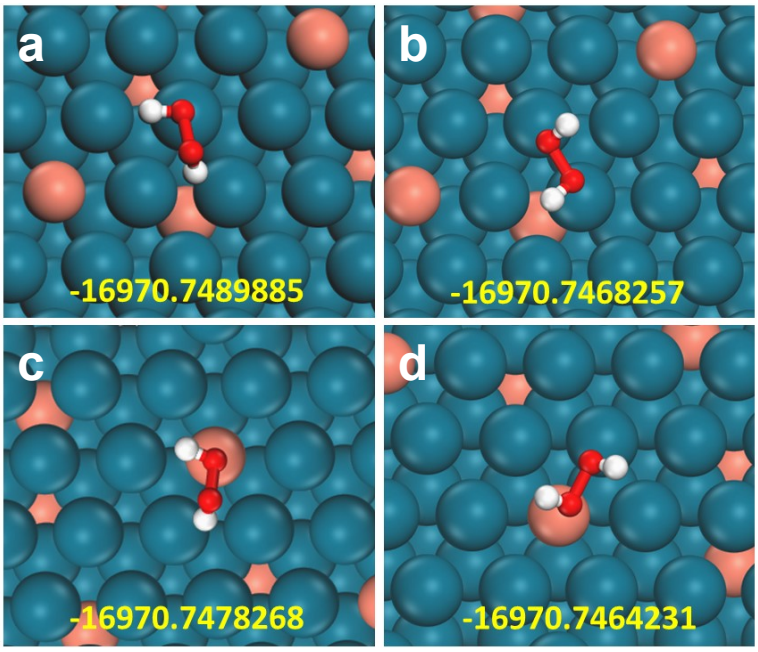

Fig. S3 Adsorptions of H_2O_2 on $Pd_{11.5}Cu$ (111) surface at Pd-top and Cu-top sites with two typical orientations: (a) H_2O_2 adsorbed on Pd with O-O tilt to the alloy surface (white, H; red, O; cyan, Pd). (b) H_2O_2 adsorbed on Pd with O-O parallel to the alloy surface. (c) H_2O_2 adsorbed on Cu with O-O tilt to the alloy surface. (d) H_2O_2 adsorbed on Cu with O-O parallel to the alloy surface. The calculated total energy (yellow text; unit: Hartree) suggests that H_2O_2 prefers to adsorb on Pd with O-O tilt to the alloy surface.

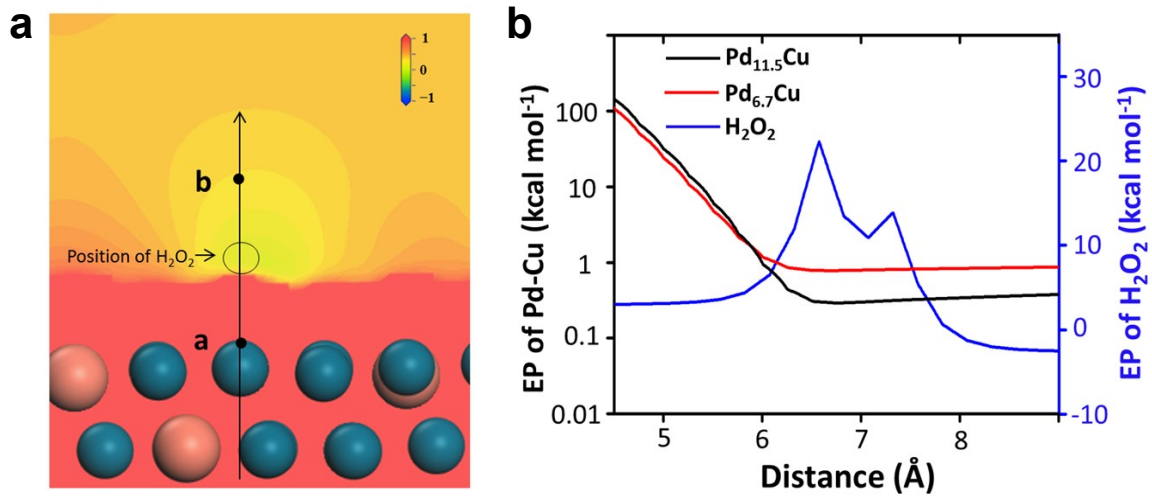

Fig. S4 (a) The EP of $Pd_{11.5}Cu$ slab model (white, H; red, O; cyan, Pd). (b) the separately scanned EP of $Pd_{11.5}Cu$, $Pd_{6.7}Cu$ and H_2O_2 along the path denoted in panel (a).

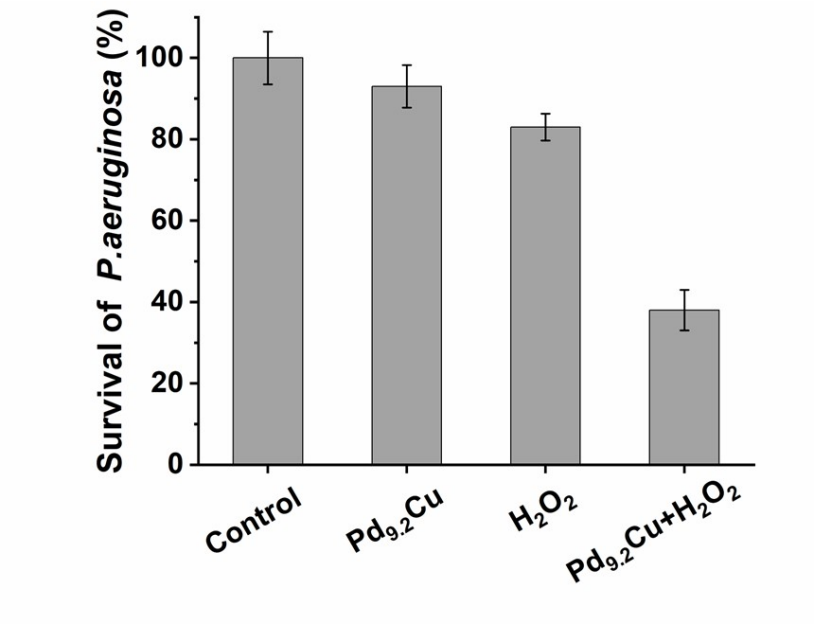

Fig. S5 Antibacterial activity of $Pd_{9.2}Cu$ NDs in killing *P. aeruginosa*.