SUPPORTING INFORMATION

Observing structure-dependent electrocatalytic activity of bimetallic Pd-Au nanorods at single-particle level

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1. Experimental section

Chemicals and Materials. Sodium borohydride (NaBH₄), hexadecyltrimethylammonium bromide (CTAB), silver nitrate (AgNO₃), HAuCl₄·3H₂O, PdCl₂ and L-ascorbic acid (AA) were purchased from Sigma-Aldrich (U.S.A). 8-Amino-5-chloro-7-phenylpyrido[3,4-d]-pyridazine-1,4[2H,3H]-dione (L012, a luminol analogue) was bought from Wako Chemical U.S.A., Inc. (Richmond, VA). 5-bromosalicylic acid, hydrochloric acid (HCl) and H₂O₂ (30%) were obtained from Sinopharm Chemical Reagent. 1M Tris-HCl buffer solution (pH 8.0) was purchased from KeyGEN Biotech (Nanjing, China). Indium tin oxide (ITO)-coated glass slides (coating thickness, ~100 nm; resistance, ~10 Ω /square) were purchased from CSG (Shenzhen, China). All reagents were used without further purification, and deionized distilled water was used throughout the experiments.

Apparatus for characterization. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were carried out on a JEOL-2100 instrument operated at 200 kV. EDX High-angle annular dark field (HAADF) STEM and STEM-EDX elemental mapping were achieved on JEM-2800 (JEOL Ltd., Japan). Scanning electron microscopy (SEM) images were obtained from S-3000 N scanning electron microscope (Tokyo, Japan). UV-vis absorption spectra were recorded on SHIMADZU UV-3600 spectrophotometer (Japan). X-ray diffraction (XRD) patterns were measured on a Rigaku Dmax 2500 PC diffractometer equipped with Cu K α radiation. Traditional electrochemical measurements were performed using CHI-660E (CH Instruments, Ins.) and MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remax Electronic Science &Technology Co. Ltd., Xi'an, China) with three-electrode system at room temperature. The Ag/AgCl and Pt wire (0.5 mm diameter) were used as the reference and counter electrodes.

ECL microscopy setup. The ECL microscopy setup was on the basis of inverted microscope (IX71, Olympus), equipped with a dark-field condenser (0.8 < NA < 0.92) and a 60X objective lens (NA 0.75). A CHI-660E electrochemical workstation was applied to control the ECL reactions. An electron multiplying CCD (EMCCD) (Andor iXon Ultra 888) with exposure time of 1s was trigged synchronously with CHI 660E by a digital delay/pulse generator. The ECL imaging was operated in a shielding room. ITO with samples immobilized on its surface was used as working electrode. The electrolyte was 300 µL 1M Tris-HCl buffer containing 1.5 mM L012 and 10 mM H₂O₂.

Preparation of Au NRs. The Au NRs were prepared following a seed-mediated growth method with little modifications.¹ Briefly, the seed solution was prepared by injecting a freshly prepared, ice-cold NaBH4 solution (10 mM, 600 μ L) into a mixture containing HAuCl₄ (10 mM, 250 μ L) and CTAB (0.1 M, 9.75 mL), followed by rapid inversion for 2 min. The resultant seed solution was kept at room temperature for 2 h prior to use.

The growth solution was prepared by dissolving CTAB (1.8 g) and 5-bromosalicylic acid (0.22 g) in 50 mL of warm water. To this solution, 0.96 mL of 0.01 M fresh AgNO₃ was added, and after keeping it undisturbed at 25 °C for 15 min, 50 mL of 1 mM HAuCl₄·3H₂O solution was added. After gentle mixing of the solution for 15 min, 0.256 mL of 0.1 M ascorbic acid was added with vigorously stirring for 30 s until the mixture became colorless. At this point, 0.16 mL of seed solution was added to the entire growth solution. The mixture was stirred for 30 s and left undisturbed at 27 °C for 12 h. The color of the growth solution slowly changed from colorless to violet. The resultant solution was centrifuged at 10000 rpm for 10 min and washed with water for three times, and achieved Au NRs were resuspended in DI water for further use. The as-made Au NRs were labeled as Au-NRs-1 and used for subsequent Pd deposition on this Au NR template. Another Au NR template, labeled as Au-NRs-2, was also made following a similar procedure except eliminating 5-bromosalicylic acid and increasing the concentration of CTAB to 0.1 M.

Preparation of Pd-tipped and Pd-covered Au NRs. H_2PdCl_4 solution (0.01 M) was prepared by dissolving 0.089 g of PdCl₂ powder in 50 mL of 0.02 M HCl solution at 60 °C. Firstly, 10 mL of above Au NRs-1 suspension was added to 10 mL of an aqueous solution containing 0.184 g of CTAB and 0.022 g of 5-BrSA. Then, 1.136 mL of 0.1 M ascorbic acid was added into 10 mL of the resulting mixture. Finally, 198 µL of 0.01 M H_2PdCl_4 and subsequently 80 µL of 0.1 M HCl were added to the reaction mixture. The mixture was left undisturbed for 12 h at 27 °C. Pd-covered Au NRs were prepared by using Au-NRs-2 as a template following the same procedure.

Synthesis of Pd-Au Janus NRs. The Pd-Au Janus NRs were synthesized follow the previously reported method with some modifications.² Firstly, the as-grown Au NR-2 solution was collected by centrifugation and washing with DI water to remove the excess surfactant. Then, the Au NRs were dispersed onto the negatively charged glass slide for 12 h through electrostatic adherence absorption. After 12h, the slide was washed with Mili-Q water carefully and dried under nitrogen atmosphere. The Au NRs modified slide was then transferred into the Electron Beam Evaporation

platform (rate of ~1 Å/s, pressure of 10^{-7} Torr) for 3nm palladium deposition. Finally, the Pd-Au Janus NRs were collected by immersing the slide into Mili-Q water under ultrasonic bath for 10 min and the solution was purified by 0.22 um filter to remove the unexpected impurities.



2. XRD patterns of representative Pd-tipped Au NRs

Figure S1. XRD patterns of a representative Pd-tipped Au NRs (black). The blue and orange curves are the standard powder diffraction patterns of the face-centered-cubic structure of Pd and the face-centered-cubic structure of Au.



3. HRTEM images and lattice diffractions of Pd-Au NRs

Figure S2. HRTEM images of Pd-coved Au NRs (A, D), Pd-tipped Au NRs (B, E) and Pd-Au Janus NRs (C, F).

4. UV-vis-NIR extinction spectra of Pd-Au NRs



Figure S3. UV-vis-NIR extinction spectra of Au NRs, Pd-tipped Au NRs and Pd-covered Au NRs.

5. CV and ECL curves of L012 and hydrogen peroxide

As in shown in Figure S4A, the ECL peak potential of L012 and H_2O_2 at Au and Pd electrode are about 0.5 V, which is lower than that on ITO and ITO-metal film electrodes. Thus, without complex physical deposition process, we could investigate the ECL behaviour of individual Pd-Au nanoparticles on conventional substrate electrodes. Moreover, at such low excitation voltage, it can reduce the passivation of the metals by electrochemical oxidation. To understand the reasons for potential resolution, we compare the CV curves of L012 (Figure S4B) and H_2O_2 (Figure S4C) at Au, Pd and ITO electrodes, respectively. Both of Au and Pd present better electrochemical activity than ITO electrodes, which could consistent with the low excitation potential and the potential resolution.



Figure S4. (A) ECL curves of 1.5 mM L012 and 10 mM H₂O₂ in pH 8.0 1M Tris-HCl buffer at ITO, ITO-Al, ITO-Ti, Au and Pd electrodes. PMT was biased at 300 V. CV curves of 1.5 mM L012 (B)

and 10mM H_2O_2 (C) in 1M Tris-HCl buffer (pH=8.0). The potential is cyclically scanned from 0 to 0.6 V at a scan rate of 50 mV/s.



6. Dark-field and ECL imaging of single NRs

Figure S5. Dark-field and ECL images of (A, E) Au NRs, (B, F) Pd-coved Au NRs , (C,G) Pd-Au Jauns NRs and (D,H) Pd-tipped Au NRs . All samples for ECL imaging were immersed in 1M Tris-HCl buffer containing 1.5 mM L012 and 10 mM H_2O_2 at pH 8.0 at 0.5 V vs. Ag/AgCl. (scale bar: 20 μ m).

7. Calculation of the heterogeneous electron transfer rate at Pd and Au electrodes

For an irreversible electrode process, the heterogeneous reaction rate constant k_0 of L012 and

H₂O₂ at Pd and Au electrodes was evaluated using equation 1.³

$$i_p = 0.227 nFACk_0 exp \left[\frac{-\alpha nF}{RT} (E_p - E_0) \right]$$
(1)

Where F is Faraday's constant (96,485 Cmol⁻¹), A is the area of electrode, $f = F/RT=38.92 V^{-1}$, α is the transfer coefficient taking as 0.5. At different scan rate, the ln(i_p) is proportional to the potential difference of (E_p-E₀) in 1.5mM L012 on Au(Figure S6A) and Pd(Figure S6B). Based the the linear relationship, k_0 can be evaluated by extending the linear region of the plots to E_p -E₀ = 0. Thus, the k_0 for the oxidation of L012 at Pd was calculated as 7.8×10⁻⁵ cm/s and2.5×10⁻⁵ cm/s at Au. Similarly, for the oxidation of H₂O₂, the k_0 at Pd was determined as 0.085cm/s and 0.004cm/s at Au.



Figure S6. The plots of ln(ip) versus (E_p-E_0) for the oxidation of L012 on the Au (A) and Pd (B) electrodes in 1.5 mM L012 solution.

8. COMSOL simulation

COMSOL Multiphysics 5.4 was employed to determine diffusive fluxs and concentration profiles of different PdAu nanostructures with three-dimensional finite element modeling.

Procedure.

"Transport of Diluted Species" physical field was used for simulating ECL reactions. In the physical field, time-dependent study on transport of diluted species was used to simulate the concentration and diffusion fluxes around the PdAu nanostructures. The inflow of the pristine substances to the electrode and the outflow of the products to the bulk solution were described below.

$$\frac{\partial C_i}{\partial t} + \nabla \cdot \left(-D_i \nabla_{C_i} \right) = R_i$$

$$N_i = -D_i \nabla_{C_i}$$
(1)
(2)

In numerical simulation, the transition conditions of redox species were follow the Fick's Second law.

$$\frac{\partial C_i}{\partial t} = D\nabla^2 C_i \tag{3}$$

Where C_i are the concentration of oxidized or reduced species, and they are the function of time and heterogeneous reaction rate k. D are diffusion coefficient and are taken as 1×10^{-5} cm₂/s for all the species. The current-potential characteristic could be described with Butler–Volmer (B-V) formalism.³

$$k_{f} = k_{0} exp[(-\alpha)f(E - E^{0})]$$

$$k_{b} = k_{0} exp[(1 - \alpha)f(E - E^{0})]$$
(5)

In this simulation, all redox and intermediate species are assumed to have no adsorption onto the nanorods, their mass transfer coefficients remain the same as those in bulk solution near the particles. Reaction 1 and 2 occurred on the electrode surface simulated in the boundary setting part. Reaction 3, 4, and 5 are occurred in the solution and simulated in the domain setting part. The innitial concentration of L012 and H_2O_2 are 1.5 mM and 10 mM respectively. The potential pulses are set at 0 V and 0.5 V with 10s time interval. Other parameters for simulations: α =0.5, R=8.31

J/(kmol), T=298 K, F=96485 C/mol, $f = F/RT=38.92 V^{-1}$.

Variables	Expression	Equation	Unit
N _{LH-}	$-D_{LH-}\nabla C_{LH-}$	$k_{f1} \times L^{-} - k_{b1} \times LH^{-}$	mol/(m ² .s)
N _L	$-D_{L}\nabla C_{L}$	$-k_{f1} \times L^{-} + k_{b1} \times LH^{-}$	mol/(m ² .s)
N _{H2O2}	$-D_{H_2O_2} \nabla C_{H_2O_2}$	$k_{f2} \times O_2 - k_{b2} \times H_2 O_2$	mol/(m ² .s)
N _{O2}	$-D_{0_2} \nabla C_{0_2}$	$-k_{f2} \times O_2 + k_{b2} \times H_2 O_2$	mol/(m ² .s)

Table S1. The molar influxes of the LH⁻, L⁻, H₂O₂ and O₂

Table S2. In the electrolyte (domain), the concontration change of the involved species with time

Chemical	Expression	Unit
LH-	$\frac{\partial LH}{\partial t} = D\nabla^2 C_{tur}$	mol/(m ³ .s)
L	$\frac{\partial L}{\partial t} = D\nabla^2 C_{L} - k_3 \times L^{-} \times O_2 - k_4 \times L^{-} \times O_2^{-}$	mol/(m ³ .s)
H ₂ O ₂	$\frac{\partial H_2 O_2}{\partial t} = D \nabla^2 C_{H_2 O_2}$	mol/(m ³ .s)
O ₂	$\frac{\partial O_2}{\partial t} = D\nabla^2 C_{O_2} - k_3 \times L^{-} \times O_2$	mol/(m ³ .s)
O ₂	$\frac{\partial O_2 - \cdots}{\partial t} = D\nabla^2 C_{O_2 -} + k_3 \times L^{-} \times O_2 - k_4 \times L^{-} \times O_2^{-}$	mol/(m ³ .s)
LO ₂ ²⁻	$\frac{\partial LO_2 2}{\partial t} = D\nabla^2 C_{LO_2 2} + k_4 \times L^{-} \times O_2^{-} - k_5 \times LO_2^{2}$	mol/(m ³ .s)

Mesh setting.

The mesh setting was extremely fine. The minimum element size is 2×10^{-11} m of PdAu nanorods.



Figure S7. Mesh setting of Pd-tipped (A), Pd-Au Janus (B) and Pd-covered Au NRs. Scar bar: 20nm

Simulation results.



Figure S8. The concentration distribution and diffusive flux diagram of H2O2 and O2 on Pd-tipped (A,D),Pd-Au Janus (B,E) and Pd-covered (C,F) Au NRs.



Figure S9. The concentration of ECL intensity on Pd-tipped(A), Pd-Au Janus(B) and Pd-covered Au NRs.

9. References

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