Electronic Supplementary Information for

Polyethyleneimine-functionalized PdOs bimetallene for enhanced oxygen reduction

Ziqiang Wang, Shan Xu, Min Li, Kai Deng, Hongjie Yu, You Xu, Xiaonian Li,

Hongjing Wang* and Liang Wang*

State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

Corresponding authors

*E-mails: hjw@zjut.edu.cn; wangliang@zjut.edu.cn

Experimental

Chemicals and Materials

Palladium (II) acetylacetonate ($Pd(acac)_2$, 99%) and Nafion (5 wt%) were acquired from Sigma-Aldrich. N,N-dimethylformamide (DMF, 99.5%), Tungsten hexacarbonyl ($W(CO)_6$, 97%), acetic acid (CH_3COOH, 99.5%), polyvinylpyrrolidone (PVP, M_w = 10000), L-ascorbic acid (AA), ethylene glycol (EG), polyethylenimine (PEI, MW = 10000) and isopropanol (99.5%) were brought from Aladdian. Osmium (III) chloride hydrate ($OsCl_3 \cdot 3H_2O$) and commercial Pt/C (20 wt%) were purchased from Alfa Aesar.

Synthesis of PdOs@PEI bimetallene

First, the Pd metallene was prepared according to the reported literature with small change [1]. In brief, 10 mg of $Pd(acac)_2$, 20 mg of $W(CO)_6$ and 8 mL of DMF were added in to a 30 mL bottle and ultrasonicated for 30 min. And then, 2 mL of acetic acid was added into the reaction mixture solution, placing in oil bath at 100 ℃ for 1 h. After the reaction, the obtained black product was collected by centrifugation and washed with ethanol completely. Then, obtanined Pd metallene was mixed with 25 mg of PVP, 25 mg of AA, and 5 mg $OsCl_3 \cdot 3H_2O$ in 8 mL EG under ultrasonication for 30 min, which was heated to 160 ℃ in an oil bath and reacted for 1 h. After that, the PdOs bimetallene was obtained after washing with ethanol for several times. For the PEI modification, 2.5 mg PdOs bimetallene with aqueous PEI solution (0.2 mg mL^{-1}, pH = 7) was stirred continuously for 30 min at 60 °C in a water bath. After centrifugation and washing, PdOs@PEI bimetallene was obtained.

Characterization

SEM images were accompanied on a ZEISS Gemini 500 SEM. TEM setup was obtained on Hitachi HT 7700. HRTEM and HAADF-STEM operated on JEOL-2100F at a voltage of 300 kV, and EDX,

SAED results were conducted in the equipment as above. Inductively coupled plasma atomic emission spectrometer (ICP-AES) was tested on Agilent 720ES. AFM was performed on NT-MDT Prima. XRD patterns were received on PANalytical X'Pert Pro MPD with Cu Kα radiation. XPS spectra were investigated using a microprobe Spectrometer (ULVAC PHI Quantera) with Al Kα radiation.

Electrocatalytic experiments

Electrocatalytic ORR measurements were performed at CHI760E electrochemical workstation installed with a three-electrode device, containing counter electrode (Pt wire), reference electrode (Ag/AgCl electrode (3 M KCl)) and working electrode (modified rotating disk electrode (RDE) with a diameter of 3 mm). For the preparation of working electrode, 2.5 μL catalyst ink was coated onto the RDE, in which catalysts were dispersed into ultrapure water, isopropanol and Nafion with a volume ratio of 8:1:1. Before ORR tests, oxygen was pumped into a 0.1 M KOH electrolyte for 30 min. Linear sweep voltammetry (LSV) was recorded by a CHI 760E electrochemical workstation at a scan rate of 0.01 V s^{-1} in range of -0.8 to 0.2 V. The cyclic voltammetry (CV) was performed in KOH solution with a rotational speed of 1600 rpm at scanning speed of 0.5 V s^{-1}. Converted all potentials to reversible hydrogen electrodes (RHE) and normalized the current density to the geometric area of the working electrode. The kinetic current was calculated according to Koutecky-Levich equation: $j_k = (j_d \times j)/(j_d - j)$, where the j_k , j_d , and j were the kinetic, diffusion limiting, and measured current density, respectively. The electrochemical active specific surface area (ECSA) was determined by CO stripping test. Firstly, CO was pumped through the 0.5 M H_2SO_4 electrolyte for 30 min, followed by flowing N_2 to remove CO from the solution, and the CV was proceeded at a scan rate of 0.02 V s^{-1} between 0 and 1.2 V. The ECSA of catalyst was calculate from the equation: ECSA = $Q/(m \times C)$, where Q denotes the charge in the oxidation area of adsorbed CO, m denotes

the Pd loading, and C denotes the charge needed for the adsorption of CO on the Pd surface as a monolayer., respectively. We carried out electrochemical impedance spectroscopy (EIS) in the frequency range of 0.1 Hz to 100 kHz in a 0.1 M KOH electrolyte.

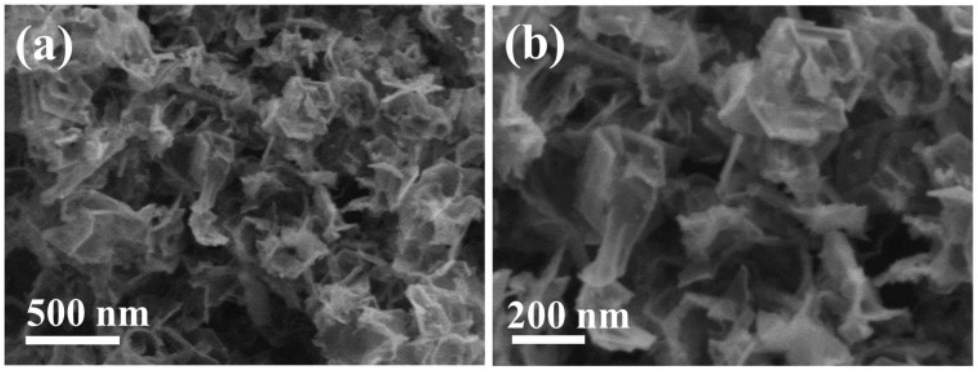

Fig. S1 SEM images of Pd metallene.

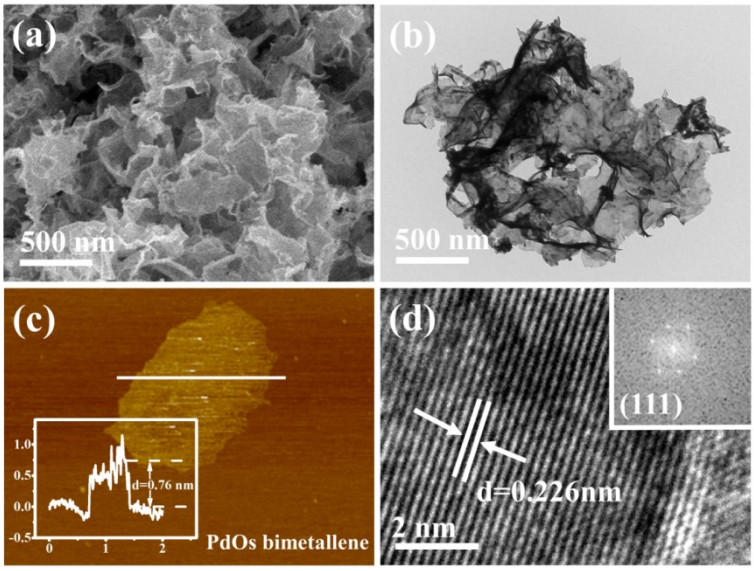

Fig. S2 (a) SEM and (b) TEM images, (c) AFM image and corresponding height profiles, and (d) HRTEM image and corresponding FFT pattern of PdOs bimetallene.

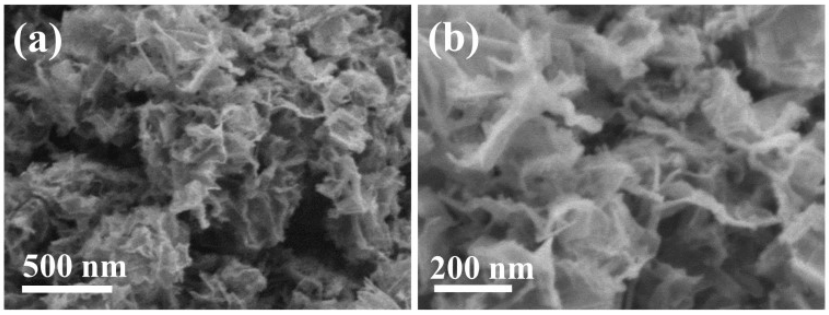

Fig. S3 SEM images of Pd@PEI metallene.

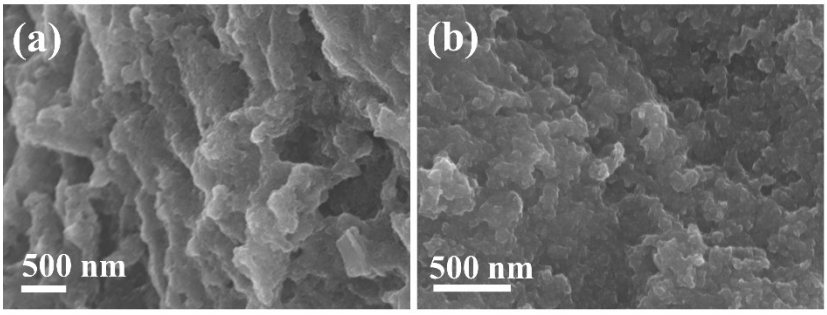

Fig. S4 SEM images of Os sample and Os@PEI sample.

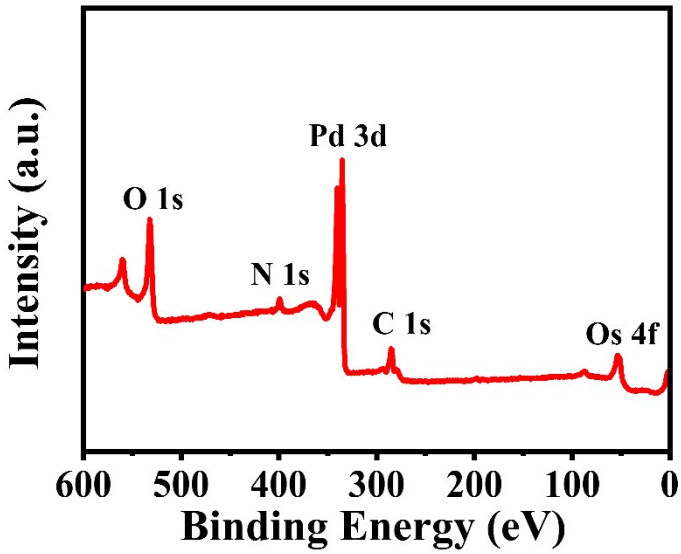

Fig. S5 XPS survey spectrum of PdOs@PEI bimetallene.

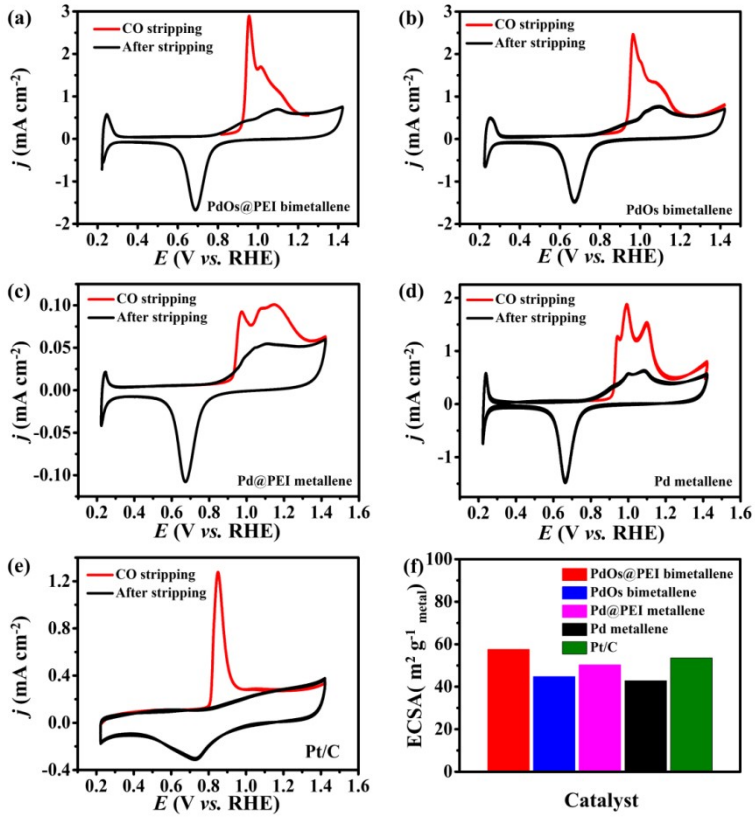

Fig. S6 CO stripping measurements of (a) PdOs@PEI bimetallene, (b) PdOs bimetallene, (c) Pd@PEI metallene. (d) Pd metallene, and (e) Pt/C in 0.5 M H_2SO_4 at a scan rate of 0.02 V s^{-1}, and (f) calculated ECSA values of various electrocatalysts from CO stripping curves.

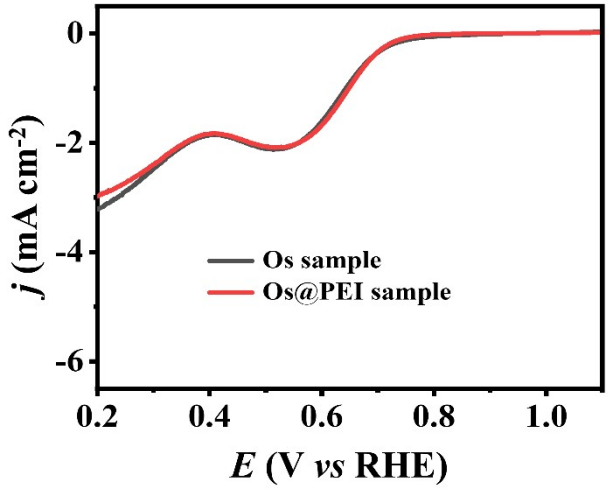

Fig. S7 ORR polarization curves of Os sample and Os@PEI sample.

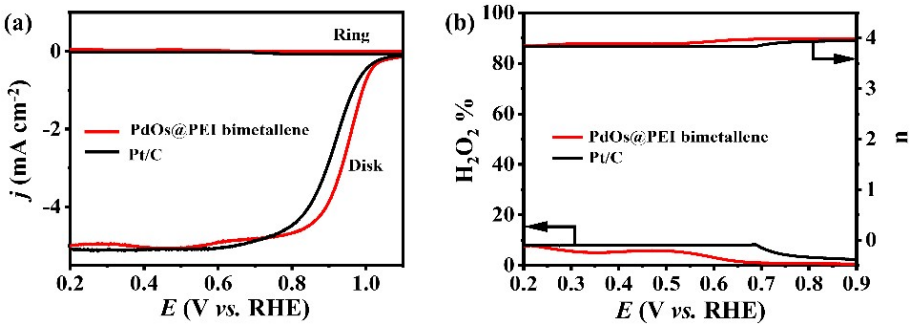

Fig. S8 RRDE tests in oxygen-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm, and (b) measured peroxide percentage and electron transfer number.

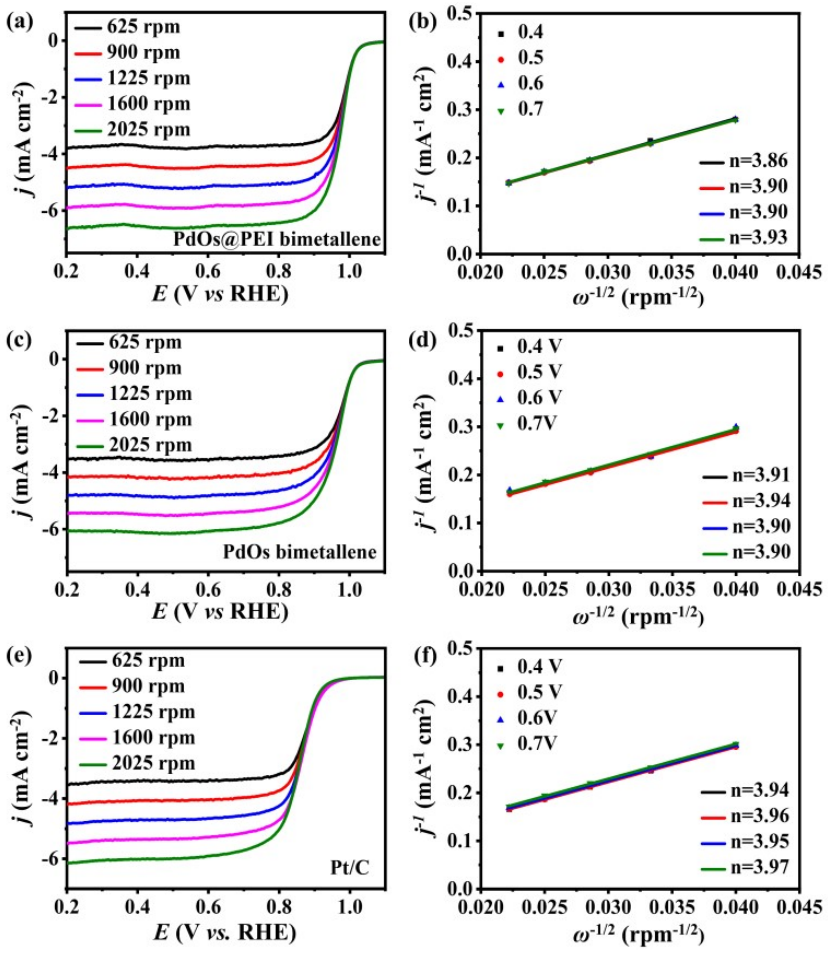

Fig. S9 (a, c, e) ORR polarization curves at different RDE rotation rates, and corresponding (b, d, f) the electron transfer numbers at different potentials.

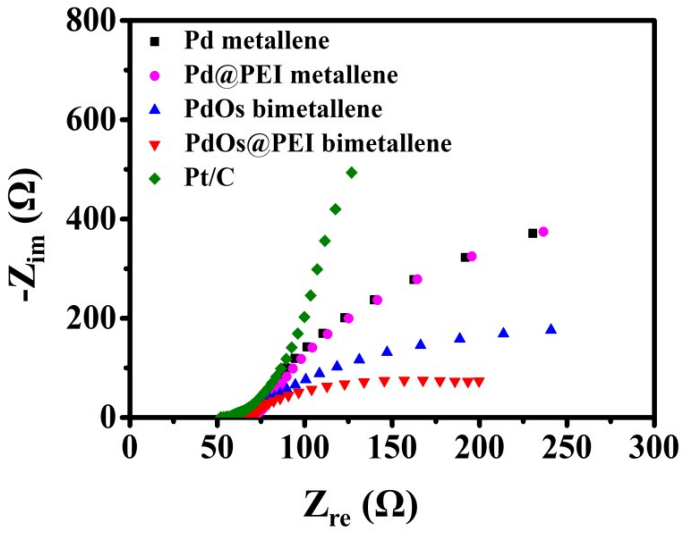

Fig. S10 Nyquist plots for the PdOs@PEI bimetallene, PdOs bimetallene, Pd@PEI metallene, Pd metallene and Pt/C recorded in an O_2-saturated 0.1 M KOH solution at 0.75 V with a rotation rate of 1600 rpm.

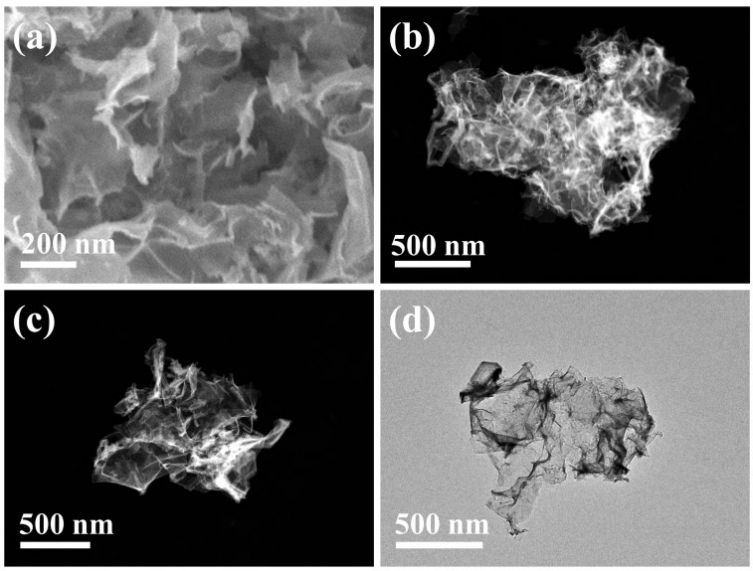

Fig. S11 (a) SEM, (b, c) HAADF-STEM, and (d) TEM images of PdOs@PEI bimetallene after stability test.

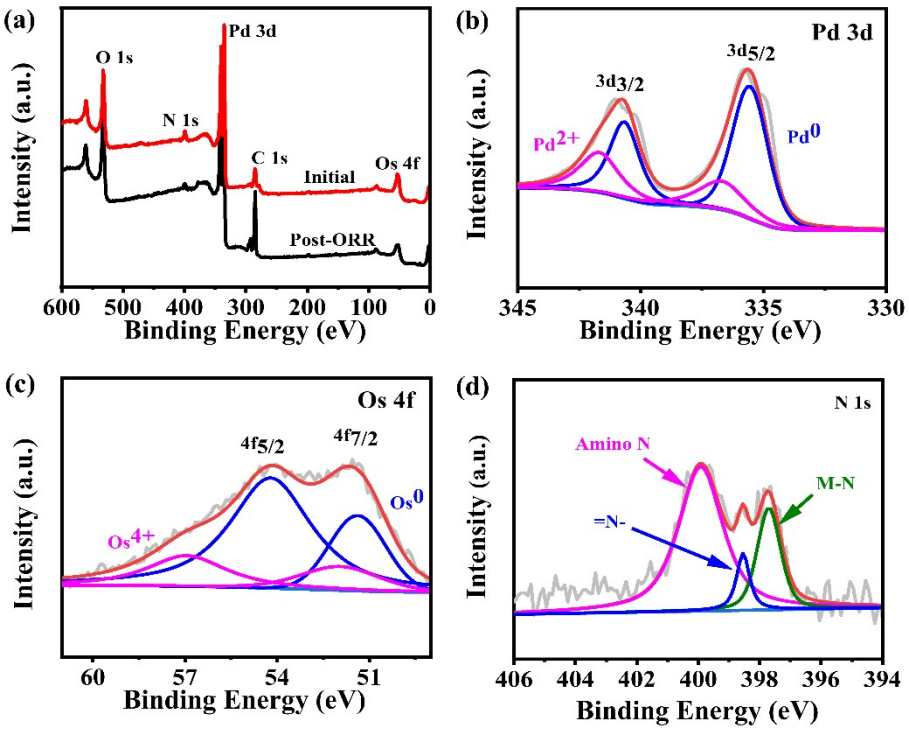

Fig. S12 (a) XPS survey spectra of initial and post-ORR PdOs@PEI bimetallene. (b) XPS spectra of Pd 3d, (c) Os 4f and (d) N 1s of the PdOs@PEI bimetallene after stability test.

Table S1 The comparisons of the ORR performance of PdOs@PEI bimetallene with published catalysts at 0.9 V.

Catalysts	Mass activities ($mA\ \mu g_{metal}^{-1}$)	Specific activities ($mA\ cm^{-2}$)	References
PdOs@PEI bimetallene	**1.29**	**2.23**	**This work**
Pd metallene/C	0.89	1.34	1
Au-NWs@Pd@PEI	0.29	/	2
Fe-Pd UPM	0.74	/	3
$Pd_9Pt_1Ni_1$ NSs	0.29	1.22	4
Pd_{NS}/WNi/C	0.5	/	5
Pd@PdFe core−shell icosahedra	0.31	1.56	6
Pd_3Pb UPINs/C	0.59	1.18	7
PdCuMo NSs	1.46	0.64	8
Pt_2Pd_1 bimetallic nanostructures	0.44	1.14	9
$PdH_{0.706}$ @Ni-B/C	1.05	/	10

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