

Supplementary Information

An exploration of the use of Au submonolayer decorated Pd₇Ir nanoparticles as highly active electrocatalyst for the ethanol oxidation reaction in alkaline media

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Experimental Section

Chemicals and materials

All the chemicals were analytical grade and used as received. Palladium chloride (PdCl_2), hydrogen hexachloroiridate hydrate ($\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$), gold chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), copper sulfate (CuSO_4), potassium hydroxide (KOH), sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were bought from Sinopharm Chemical Reagent Co. Ltd, China. Carbon support (Vulcan XC-72, 20–40 nm) was acquired from E-TEK and 20 wt.% Nafion solution was from DuPont. All aqueous solutions were prepared with deionized (DI) water.

Synthesis of $\text{Pd}_7\text{Ir}/\text{C}$ and Pd/C electrocatalysts

The Pd/C and $\text{Pd}_7\text{Ir}/\text{C}$ electrocatalysts were synthesized using a co-reduction method. The precursor solution including PdCl_2 and $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$ was firstly mixed together according to the optimal Pd/Ir atomic ratio of 7:1. Vulcan XC-72 carbon support was then ultrasonically suspended in the above solution under vigorous stirring for 30 minutes. Subsequently, 2 wt.% NaBH_4 solution was added into the mixture and kept continuously stirring for another 5 hours. The final products were collected by filtration after complete reaction, washed several times by DI water and dried at 60 °C in an oven for 12 hours. The as-prepared samples were guaranteed with a 20 wt.% metal loading and stored for further use. Pd/C was prepared following the same procedure but without adding $\text{H}_2\text{IrCl}_6 \cdot x\text{H}_2\text{O}$.

Preparation of $\text{Pd}_7\text{Ir}@/\text{Au}/\text{C}$ electrocatalysts

The Au submonolayer modified $\text{Pd}_7\text{Ir}/\text{C}$ electrocatalyst ($\text{Pd}_7\text{Ir}@/\text{Au}/\text{C}$) was carried out using Cu underpotential deposition (UPD) coupled with Au^{3+} galvanic displacement. To be specific, a catalyst ink of $\text{Pd}_7\text{Ir}/\text{C}$ was prepared by suspending 10 mg sample in 2 mL ethanol ultrasonically. 8 μL of the as-prepared ink was piped onto the glassy carbon electrode (GCE, 0.1256 cm^2) to guarantee the metal loading to be 64 $\mu\text{g}/\text{cm}^2$. A platinum coil and a saturated calomel electrode (SCE) serve as counter

electrode and reference electrode, respectively. It is noted that the deposition potential and Cu bulk deposition potential was normalized to reversible hydrogen electrode (RHE), which should be distinguished from the EOR measurements in alkaline media. After totally being dried in air, the electrode was transferred into the pre-mixed solution of 50 mM CuSO_4 and 50 mM H_2SO_4 saturated with Ar and a potential sweep between 0.353 V to 0.763 V (vs. RHE) was continuously applied to remove the residuals on the surface of Pd_7Ir nanoparticles (NPs). After that, a linear anodic potential sweep was conducted on the as-treated electrode to 0.763 V to remove all the Cu atoms adsorbed on the $\text{Pd}_7\text{Ir}/\text{C}$ NPs. Subsequently, Cu monolayer was deposited onto the $\text{Pd}_7\text{Ir}/\text{C}$ NPs through a cathodic scan from 0.763 V to 0.353 V. The scan rate for all the above operations are 20 mV/s. Thereafter, the Cu-modified electrode was immediately immersed in the Ar-saturated solution of 50 mM HAuCl_4 and 50 mM H_2SO_4 for 3 minutes in order to completely displace Cu by Au. Finally, $\text{Pd}_7\text{Ir}@\text{Au}/\text{C}$ electrocatalyst with an Au submonolayer (2/3 surface coverage) was successfully synthesized.

Characterizations of physiochemical properties

The X-ray diffraction (XRD) measurements of Pd/C and $\text{Pd}_7\text{Ir}/\text{C}$ electrocatalysts were tested on a D8 ADVANCE Da Vinci Poly-functional X-Ray Diffractometer, using a Cu $\text{K}\alpha$ source operating at 40keV at a scan rate of $0.025^\circ/\text{s}$ from 10° to 90° . The Pd 3d X-ray photoelectron spectroscopy (XPS) spectra for Pd/C and $\text{Pd}_7\text{Ir}/\text{C}$ was acquired from a Shimadzu Kratos AXIS UltraDLD X-ray photoelectron spectroscopy instrument. The transmission electron microscopy (TEM) images were obtained from a JEOL JEM-2100F field emission microscope. The high-angle annular dark field scanning TEM (HAADF-STEM) images and STEM energy dispersive spectroscopy (STEM-EDS) elemental mapping tests were both obtained from a JEM-ARM200F spherical aberration correction transmission electron microscope.

Measurements of electrochemical properties

The electrochemical measurements of all the above as-synthesized electrocatalysts were tested in a conventional three-electrode cell linked with a

potentiostat (PGSTAT302N, Metrohm Autolab). The platinum coil was the counter electrode and the Mercuric Oxide Electrode (Hg/HgO/KOH (1.0 mol/L), MMO), which was connect to the cell through a Luggin capillary, performed as a reference electrode for the ethanol oxidation reaction (EOR) tests in alkaline media. The glassy carbon electrode (GCE, 0.1256 cm²) used for electrochemical measurements was the same as that used for Cu-UPD in the former section and was polished delicately as the working electrode. For Pd₇Ir/C and Pd/C, the preparation of catalyst ink on GCE follows the same procedure as that in Cu UPD in order to guarantee the metal loading on GCE to be 64 µg/cm². The as-prepared Pd/C, Pd₇Ir/C and Pd₇Ir@Au/C samples on GCE were at last piped 8 µL of diluted Nafion solution (0.02 mL 20 wt.% Nafion mixed with 1.98 mL ethanol) on the electrode as binder for further electrochemical tests.

All the following electrochemical tests were all operated at a scan rate of 50 mV/s ranging from -0.856 V to 0.274 V vs. MMO. The test to determine the change of CV curves before and after Au deposition for Pd₇Ir/C is tested in 1 mol/L KOH without current density normalization. The EOR catalytic activity in alkaline media was conducted in a mixed solution of 1mol/L KOH and 1mol/L ethanol. And the degradation measurements were conducted by two steps: 3000 cycles sweep was performed 1 mol/L KOH solution. Then, the resulting EOR curves were recorded in the mixed solution of 1 mol/L KOH and 1 mol/L ethanol. It is noted that the current for Pd₇Ir@Au/C was normalized to the same noble metal loading as 64 µg/cm² and all the above-mentioned current densities were normalized to the geometric area of the GCE.

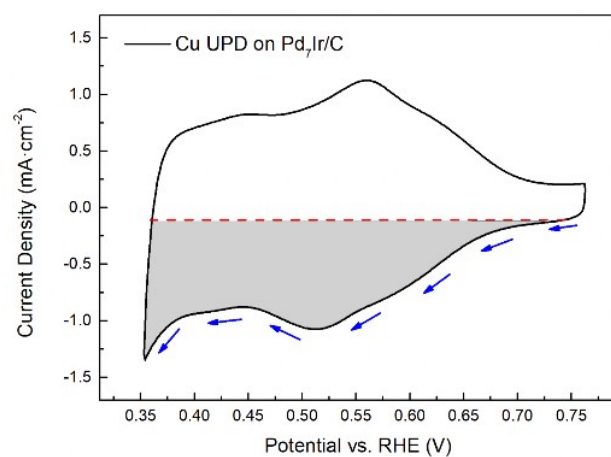


Fig. S1 CV curves of the Cu UPD for the Pd₇Ir/C electrocatalyst. The series of blue arrows represent the specific diagram when conducting Cu UPD. Area marked in grey represents the total Cu adsorption region. (Electrolyte: 50 mM H₂SO₄+ 50 mM CuSO₄, scan rate: 20 mV/s, scan range: 0.353 to 0.763 V vs. RHE)

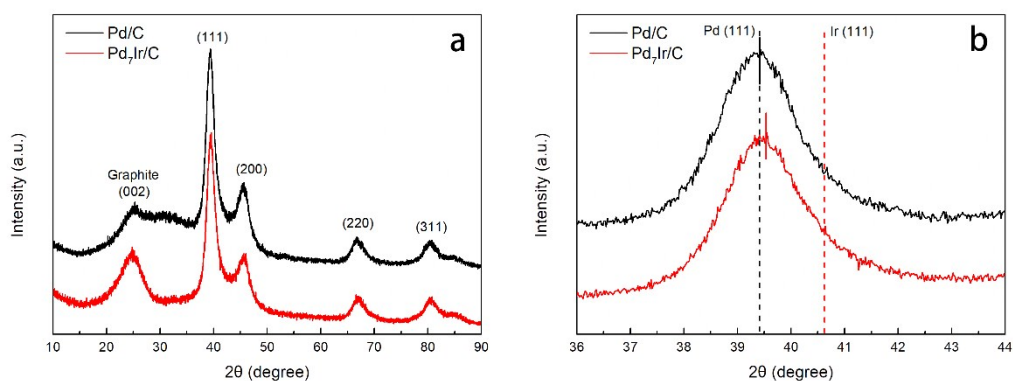


Fig. S2 XRD patterns (a) and magnified (111) peak (b) for Pd/C and Pd₇Ir/C

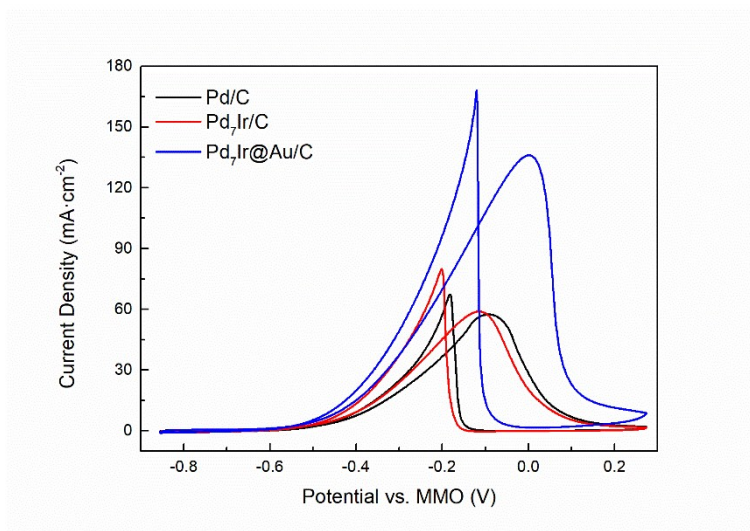


Fig. S3 Overall cyclic voltammograms for the Pd/C Pd₇Ir/C and Pd₇Ir@Au/C electrocatalysts in 1 mol/L KOH + 1 mol/L ethanol (scan rate: 50 mV/s)

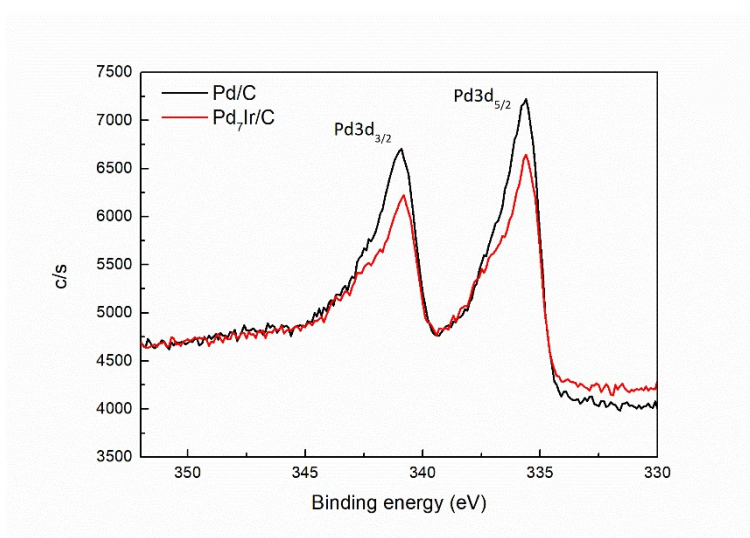


Fig. S4 Pd 3d XPS spectra for Pd/C and Pd₇Ir/C