

SUPPORTING INFORMATIONS

Heteroepitaxial Interface of Pt//CeO₂ Nanoparticles for Enhanced Catalysis in Oxygen Reduction Reaction (ORR)

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Materials Characterization

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The Pt and Ce content was quantified by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Agilent5800, Agilent Technologies). 1.7 mg of sample was weighed and transferred to a quartz beaker. 5 mL H₂SO₄ and a few drops of HNO₃ were added to the beaker and the beaker was heated until bubbling stopped. 3 mL of HCl then added to the beaker to dissolve the residues by heating. After cooling, the obtained solution was transferred to a 100 mL volumetric flask. 10 mL of 20 mg/L Mn standard solution which is used as internal standard element for ICP-AES was added to the flask and then the solution was diluted to the marked line with Milli-Q water (pure water).

Table S1. Composition of Pt and Ce obtained from ICP-AES showed a Pt: Ce molar ratio of 2:1. This value indicates an excess of Ce compared to the expected Pt:Ce ratio of 5:1 for Pt₅Ce nanocrystals suggesting the sample contains not only Pt₅Ce nanocrystals but also Ce-rich impurity phases.

	Pt	Ce
Mass %	9.7	3.49
mole	2	1

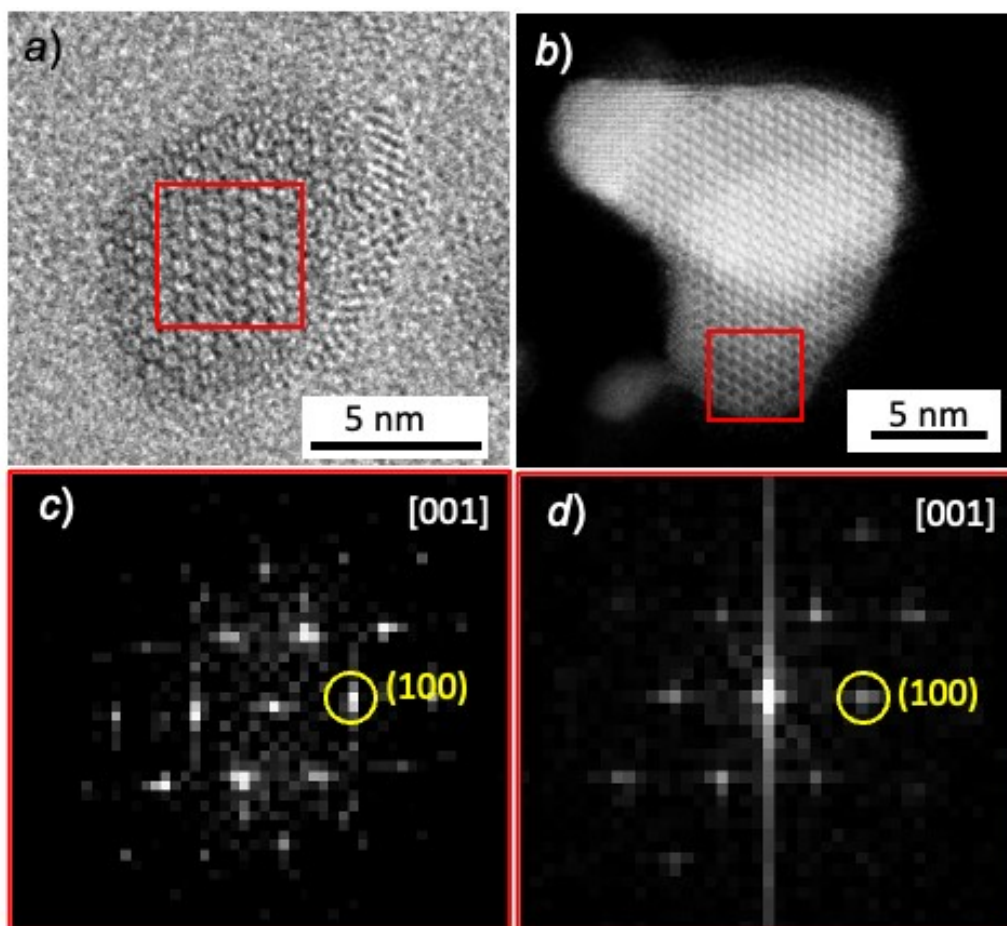


Fig. S1. *a)* TEM image and *b)* HAADF-STEM image of Pt₅Ce nanocrystals, *c-d)* FFT patterns from the red squares corresponding to particles in Fig. S1*a-b*. Measurement of the interplanar spacing (0.47 nm) confirmed the successful synthesis of Pt₅Ce nanocrystals.

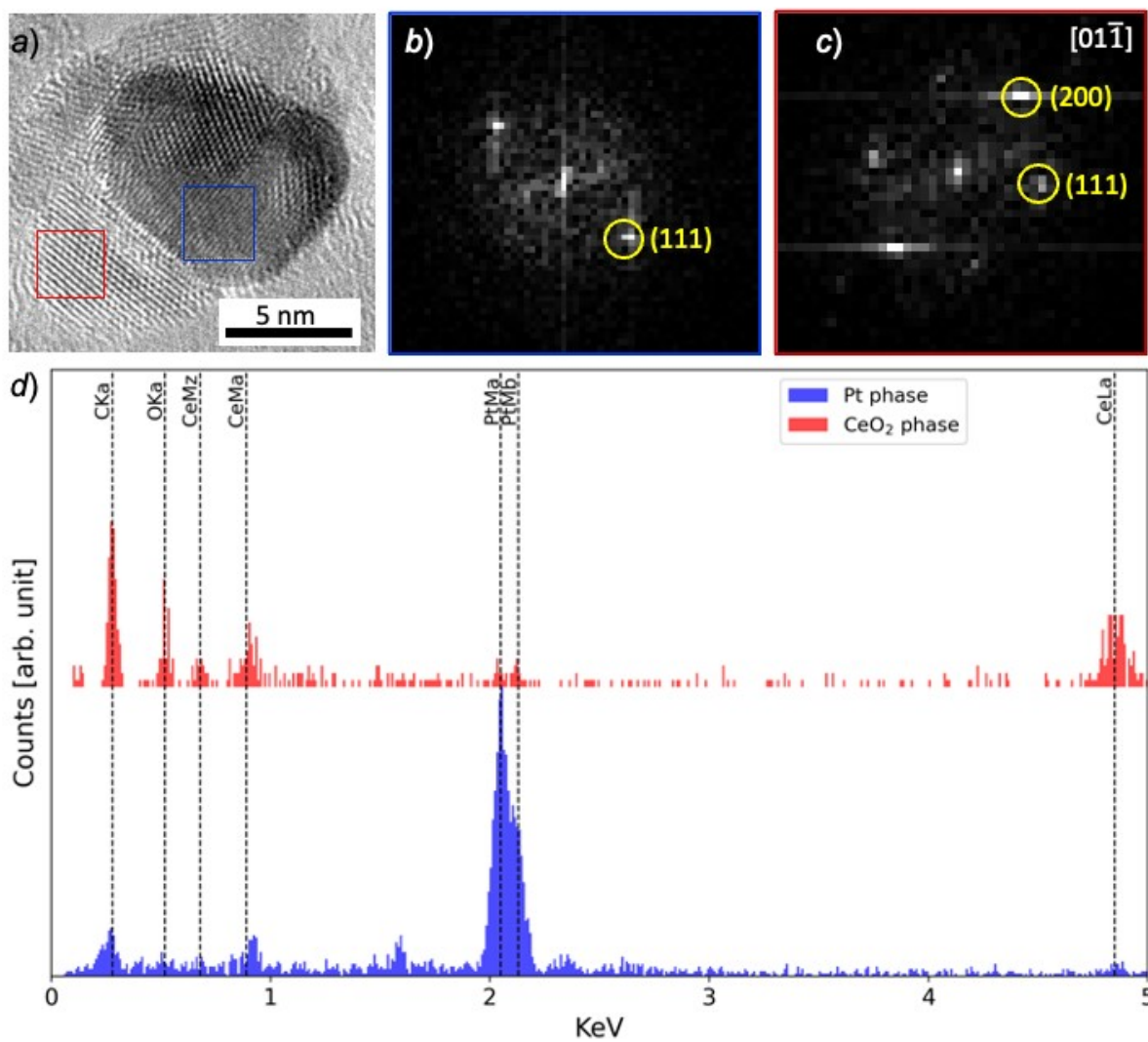


Fig. S2. *a)* TEM image of Pt//CeO₂ nanoparticles after phase separation, *b-c)* FFT patterns for the blue and red squares, indicating that they correspond to Pt and CeO₂, respectively. *d)* EDS-spectra showing that the region at the blue square (lower) consist of Pt mainly and the region around the red one (upper) contains larger amount of oxygen and Ce relatively to Pt, confirming phase separation has indeed completed.

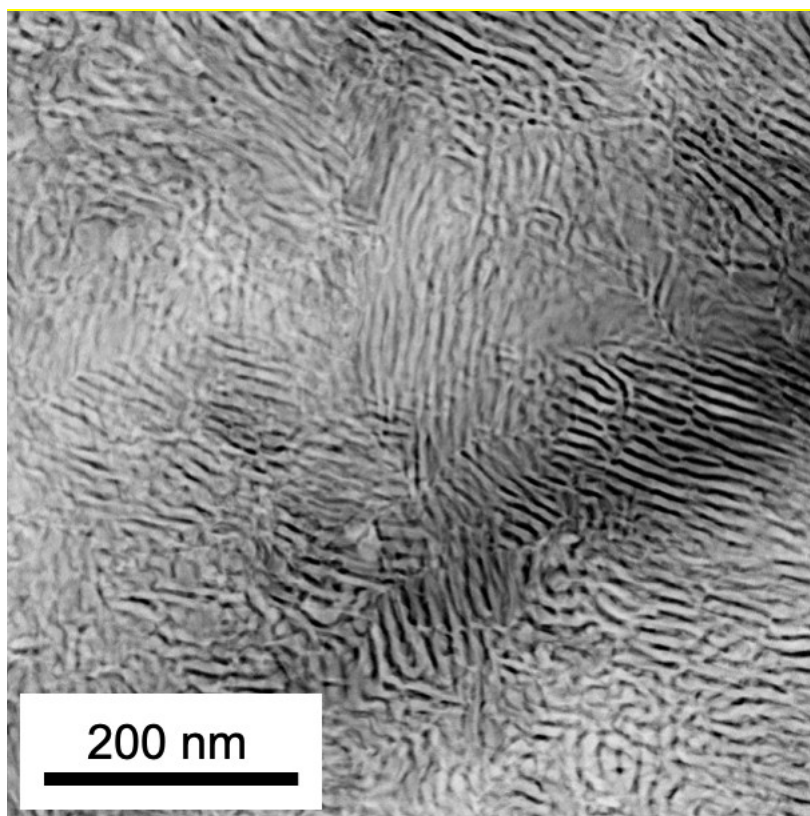


Fig. S3. Cross-section HAADF-STEM image of a phase-separated Pt//CeO₂ bulk particle (particle size $\sim 50 \mu\text{m}$). The dark- and bright contrasted stripes correspond to the CeO₂- and Pt phases, respectively. The Pt- and CeO₂ phases are grafted to form a heteroepitaxial Pt(111)//CeO₂(111) interface, as reported in ref.19. The Pt//CeO₂ material was prepared by heating mechanically-powdered Pt₅Ce alloy ingot in a stream of mixture gas consisting of CO (10 ml/min) and O₂ (5 ml/min) at 600 °C for 12 hours.

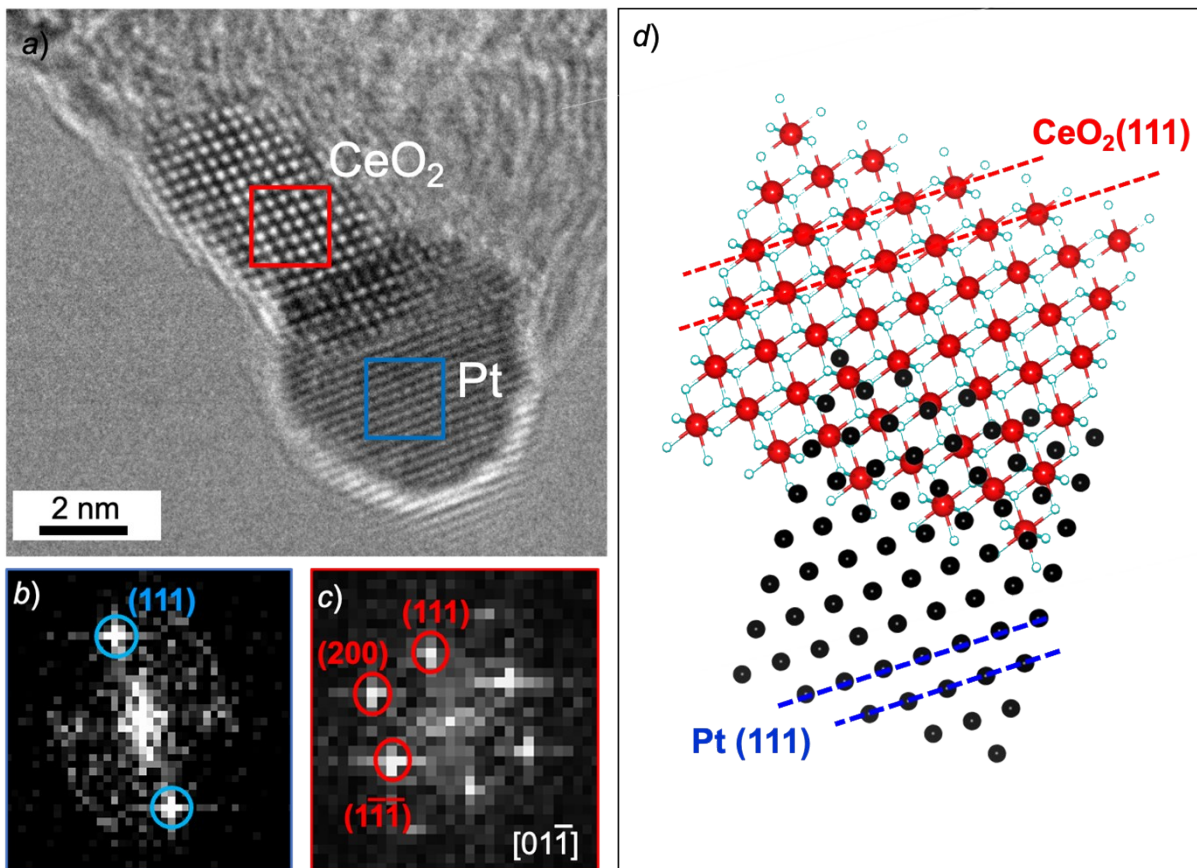


Fig. S4. *a)* TEM image of a Pt//CeO₂ nanoparticle with an epitaxial interface. *b-c)* FFT patterns show the epitaxial interface of Pt (111)//CeO₂(111) *d)* Schematic illustrating of Pt (111)//CeO₂ (111) interface relationships.

ECSA evaluation

The electrochemical surface area (ECSA) is calculated based on the formula where:

$$\text{ECSA} = \frac{Q_H}{0.21 \times [\text{Pt}]}$$

Q_H is the hydrogen desorption charge from CV, 0.21 mC cm^{-2} is electrical charge associated with hydrogen desorption on Pt surface and $[\text{Pt}]$ is loading weight of Pt on electrode. The Pt//CeO₂ nanoparticles had ECSA of $9.0 \text{ cm}^2 \text{ gPt}^{-1}$ compared to the Pt//CeO₂ bulk catalyst, $29 \text{ cm}^2 \text{ gPt}^{-1}$.

To convert the potentials obtained with the Ag/AgCl electrode to the RHE (Reversible Hydrogen Electrode) scale, we employed the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl}} + 0.059 \times \text{pH}.$$

Here, E_{RHE} is the potential on the RHE scale, $E_{\text{Ag/AgCl}}$ is the potential measured against the Ag/AgCl electrode, $E^{\circ}_{\text{Ag/AgCl}}$ is the standard potential of the Ag/AgCl electrode, and $+0.059 \text{ V}$ is the Nernstian shift per pH unit at room temperature (25°C). The pH of the 0.1 M KOH electrolyte solution was 13.

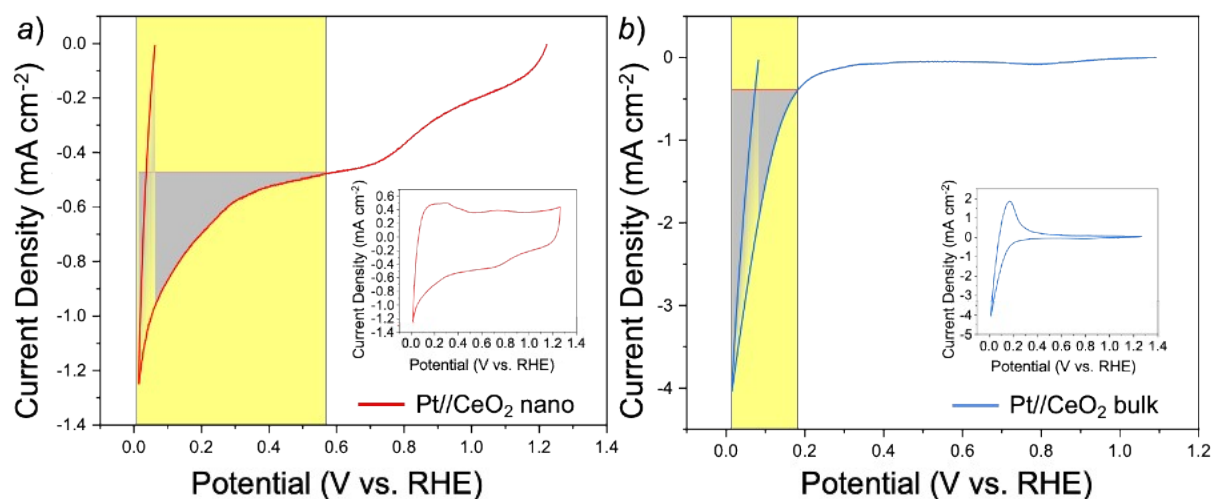


Fig. S5. ECSA calculated from integration of hydrogen desorption peak in the CV curves of a) the Pt//CeO₂ nanoparticles and b) the Pt//CeO₂ bulk catalyst. CVs were taken in 0.1 M KOH with a scan rate at 20 mV/s . The potential was referenced against an Ag/AgCl electrode and then converted to the values for the reversible hydrogen electrode (RHE) for better readability.

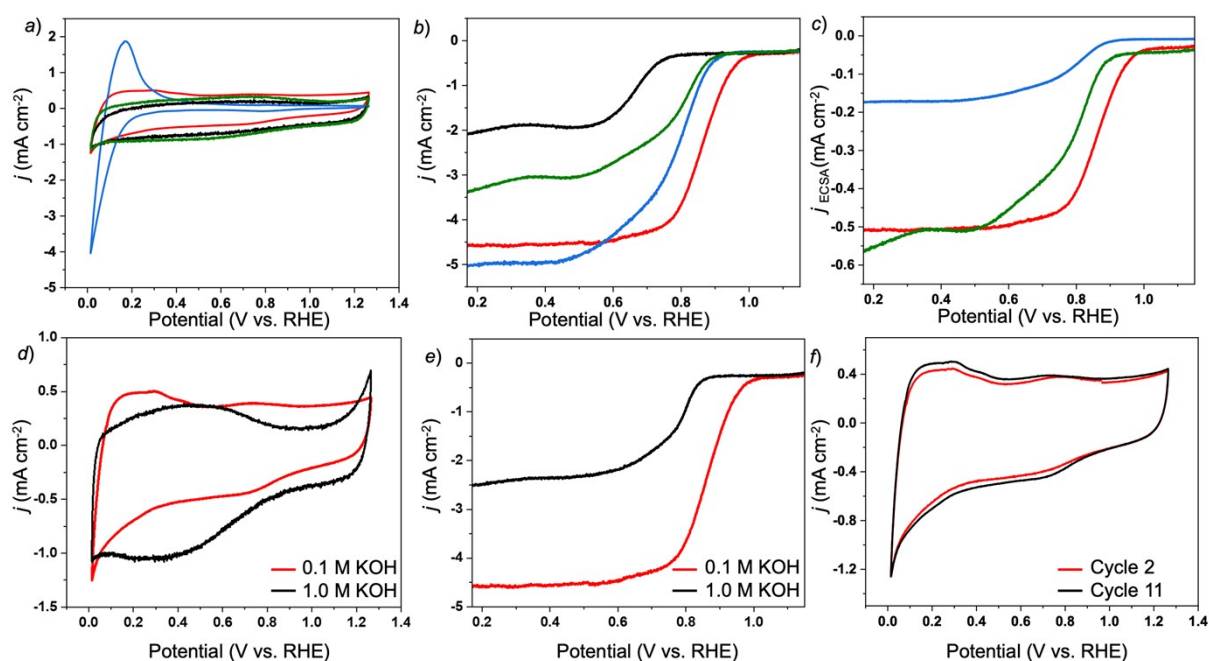


Fig. S6. *a*) Cyclic Voltammetry (CV) in Ar-saturated 0.1 M KOH, *b*) Linear sweep voltammetry (LSV), *c*) LSV normalized ESCA showing comparison of electrochemical performance of Pt₅Ce nanocrystals, Pt//CeO₂ nanoparticles, Pt//CeO₂ bulk particles and graphene nanoplatelets (represents by green, red, blue and black curves). *d*) CV in Ar-saturated, *e*) LSV of Pt//CeO₂ nanoparticles in different pH conditions of 0.1 M KOH and 1.0 M KOH and *f*) Stability test of Pt//CeO₂ nanoparticles in 0.1 M KOH.

Table S2. Summary of electrochemical parameters.

Catalysts	E_{onset} (V vs. RHE)	Ref.
Pt-CeO ₂ @CN	0.954	23
Pt(110)//CeO ₂ (110) nanoparticles	1.01	This work
Pt(111)//CeO ₂ (111) bulk particles	0.91	This work

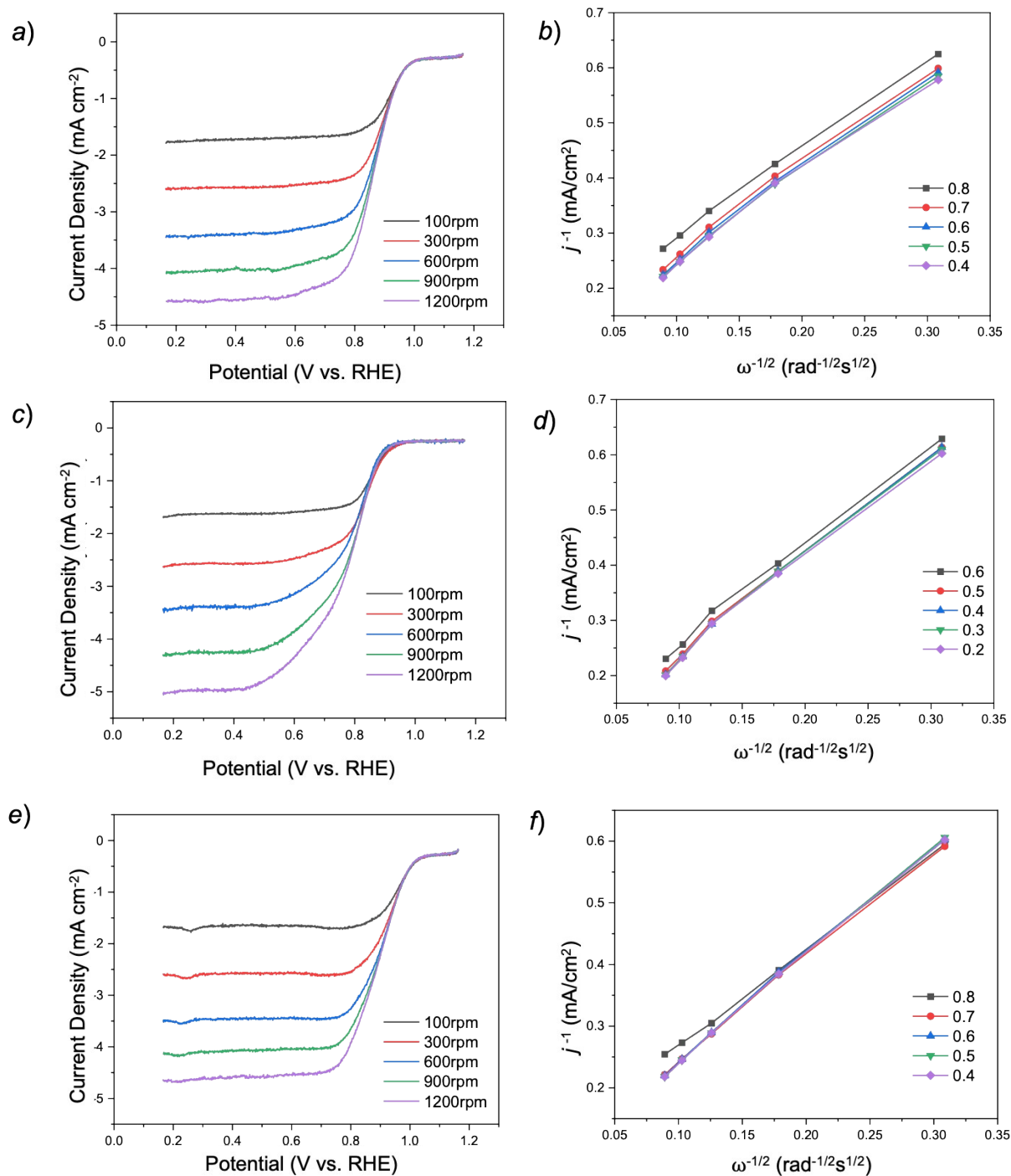


Fig. S7. The rotation-rate-dependent current-potential curves and Koutecky-Levich (K-L) plots at different potentials for (a-b) the Pt//CeO₂ nanoparticles, (c-d) the Pt//CeO₂ bulk catalyst, and (e-f) Pt/C (Fuel Cell Store, Inc., Pt loading weight=20 %). The potential was referenced against an Ag/AgCl electrode and then converted to the values for the reversible hydrogen electrode (RHE) for better readability.

The electron transfer number (n) was obtained from the Koutechy-Levich (K-L) equations:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

$$B = 0.62nFC_oD_o^{2/3}\nu^{-1/6}$$

Where F is the Faraday's constant (96485 C/mol), C_o is the bulk concentration of O_2 , to (1.2×10^{-6} mol/cm for 0.1 M KOH), D_o is the diffusion coefficient of O_2 , (1.9×10^{-5} cm/s) and ν is the kinetic viscosity of the 0.1 M KOH (0.01 cm²/s).

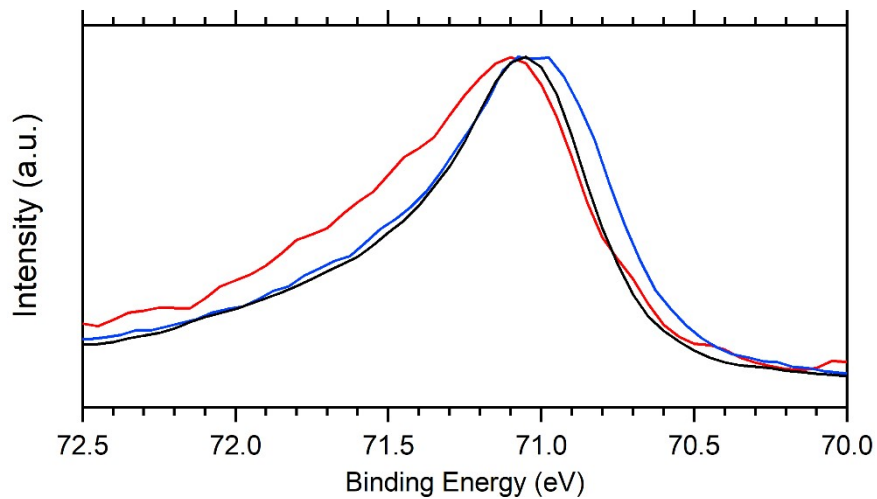


Fig. S8. HAXPES spectra of Pt $4f_{5/2}$ region. The red, blue, and black curves correspond to the Pt//CeO₂ nanoparticles, the Pt//CeO₂ bulk catalyst, and pure Pt bulk, respectively. The Pt $4f_{5/2}$ emission peak for the Pt//CeO₂ nanoparticles shows 74 meV downward shift compared to that for the Pt//CeO₂ bulk catalyst and pure Pt bulk.