

Supplementary Information

Promotion of ceria-modified Pt-Au/C cathode catalysts for oxygen
reduction reaction by H₂-induced surface segregation

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Experimental section

1. Preparation of Catalysts

10 wt % Pt₅₀Au₅₀/C catalysts were prepared by the precipitation-deposition method and modified by 15 % CeO₂. Aqueous solutions of PtCl₄ (Merck), HAuCl₄ (Aldrich) with Ce(NO₃)₃ (Fluka) in the desired stoichiometry were mixed and co-deposited at 340 K onto the commercial carbon black (Vulcan XC-72R) at pH = 7 – 9. The as-deposited catalysts were subsequently stirred at 298 K for 24 h, washed, dried at 320 K for 24 h, reduced in flowing H₂/N₂ (10/90 vol%) gas at 470 K for 1 h and stored as fresh PtAu/Ce₁₅C catalysts. For further promotion of the electrochemical performance, the fresh catalysts denoted as Pt-Au were heat treated for 1 hr at given temperatures under flowing H₂ gas at a flow rate of 70 mL min⁻¹. The alloy catalysts treated at 520, and 620 K were designated as H520, and H620, respectively.

2. Characterization of Catalysts

Physical properties of the fresh and heat-treated catalysts were characterized by XRD. A Guinier powder diffractometer (Huber, Germany), set at 45° transmission angle, was used in this work. A Johansson-type Ge monochromator produces a focused high-intensity monochromatic CuKα1 primary beam ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 20 mA. In the preparation of each sample, a small amount of catalyst was slightly pressed to a thin pallet of 0.3 mm thickness. This pellet was then fixed between two 3 μm polyethylene foil into the sample holder under ambient conditions. The XRD was operated at a scan rate of 1°/min. Scherrer's formula was accustomed to estimate the particle size of alloy nanoparticles. The morphology of the alloy catalysts were examined by a Jeol-2100 high resolution transmission electron microscope (HRTEM) with a LaB₆ electron gun source operated at 200 KeV. [Scanning transmission electron microscopic \(STEM\) was carried out with a Jeol-2100 TEM equipped with an EDX attachment \(Oxford\) to obtain the line-scan information on the compositional variations across the nanoparticles.](#) Surface species of alloy catalysts were analyzed by the TPR. The pre-oxidized (300 K for 1 h) catalysts with oxygen chemisorbed monolayers on

their surface were reduced by a flow of 10 % H₂ in N₂ while raising the temperature from 140 to 400 K at a heating rate of 7 K min⁻¹. Temperature variations on the hydrogen consumption were detected by a thermal conductivity detector (TCD). An XPS (Thermo VG Scientific Sigma Probe) using a monochromatic X-ray source (Al K α) was performed to study the surface compositions of the alloy catalysts. The powder samples were delivered to an ultra high vacuum system (UHV, SPECS GmbH) for analysis by XPS. The surface compositions of the catalysts were estimated by calculating the integral of each peak. Shirley type background was used to subtract the original peak and then a combination of Lorentzian and Gaussian lines was applied to fit the experimental curve. Accurate binding energies were determined by referencing to the C 1s peak at 284.6 eV.

Electrochemical measurements were conducted by a glassy carbon rotating disk electrode (RDE), a MSR rotator (Pine Instrument) and a microcomputer-controlled electrochemical analyzer (CHI700a, CH Instrument). The alloy catalysts in 2-propanol were dispersed in ultrasonic bath, blended with diluted Nafion solution (5 wt%, DuPont), and then deposited onto the glassy carbon RDE (0.19625 cm² area). [The final loading of noble metal on the electrode was controlled to 40 \$\mu\$ g for both the commercial Pt/C and various Pt–Au alloy catalysts.](#) A 0.5 M H₂SO₄ (Panreac) aqueous solution was used as the electrolyte, and saturated with high-purified O₂ (99.999 %) at room temperature. A Pt plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Prior to each electrochemical measurement, the electrodes were cycled several times between -0.24 and 0.96 V (vs. SCE), to produce clean surfaces at a scan rate of 20 mV s⁻¹ and a rotation rate of 1600 rpm. Linear sweep voltammetry (LSV) with a scan rate of 5 mV s⁻¹ and a rotation rate of 1600 rpm was also applied. All potentials in this study are given with respect to the reference electrode, which is +0.241 V vs. NHE. The Pt/C (20 wt %, E-TEK) catalyst was also compared in this study.

Table S1† XPS, TPR, and electrochemical characterizations of Pt-Au and H₂-treated Pt-Au catalysts. For TPR analysis, the samples were pre-oxidized at 300 K.

Catalyst	XPS composition (%)						TPR species	I ₀₈ (mAcm ⁻²)
	Pt: Au	Pt(0)	Pt(II)	Pt(VI)	Au(0)	Au(III)		
Pt-Au	80.0:20.0	28.9	41.4	9.7	15.8	4.2	A ^{Pt}	0.5
H520	68.7:31.3	34.4	28.0	6.3	27.2	4.1	A ^{Pt}	1.4
H620	61.9:38.1	50.1	11.2	0	35.8	2.3	Au	0.7

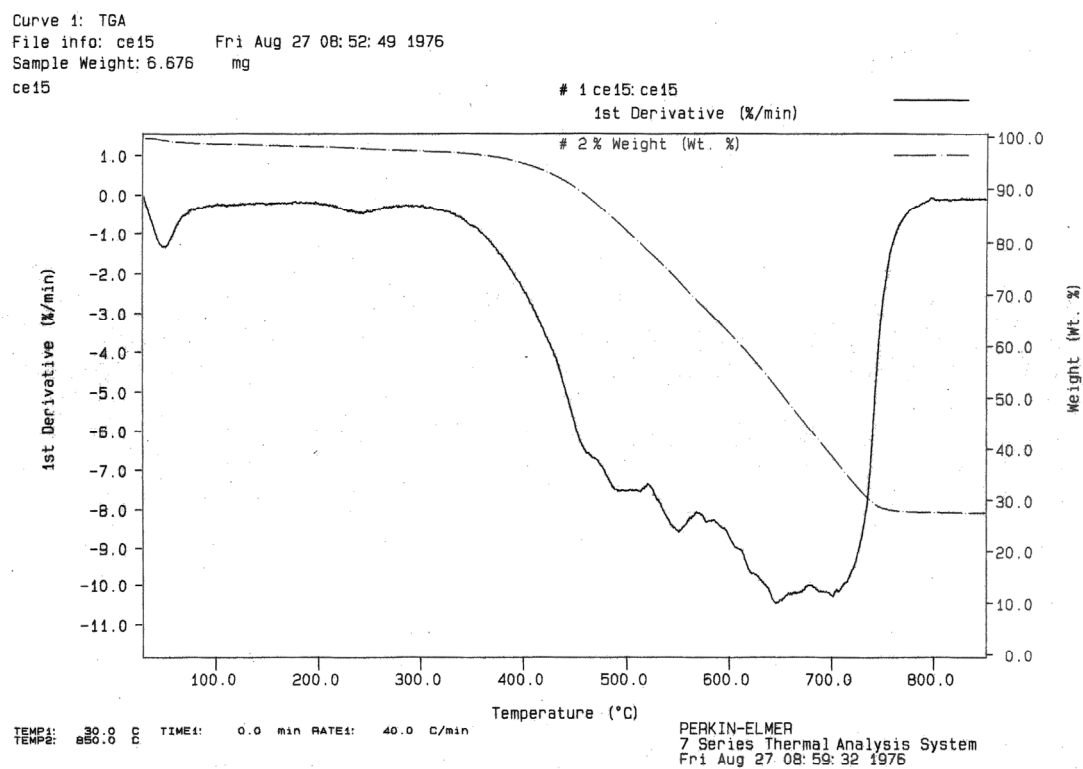


Figure S1† The TGA curve of Pt-Au catalyst.

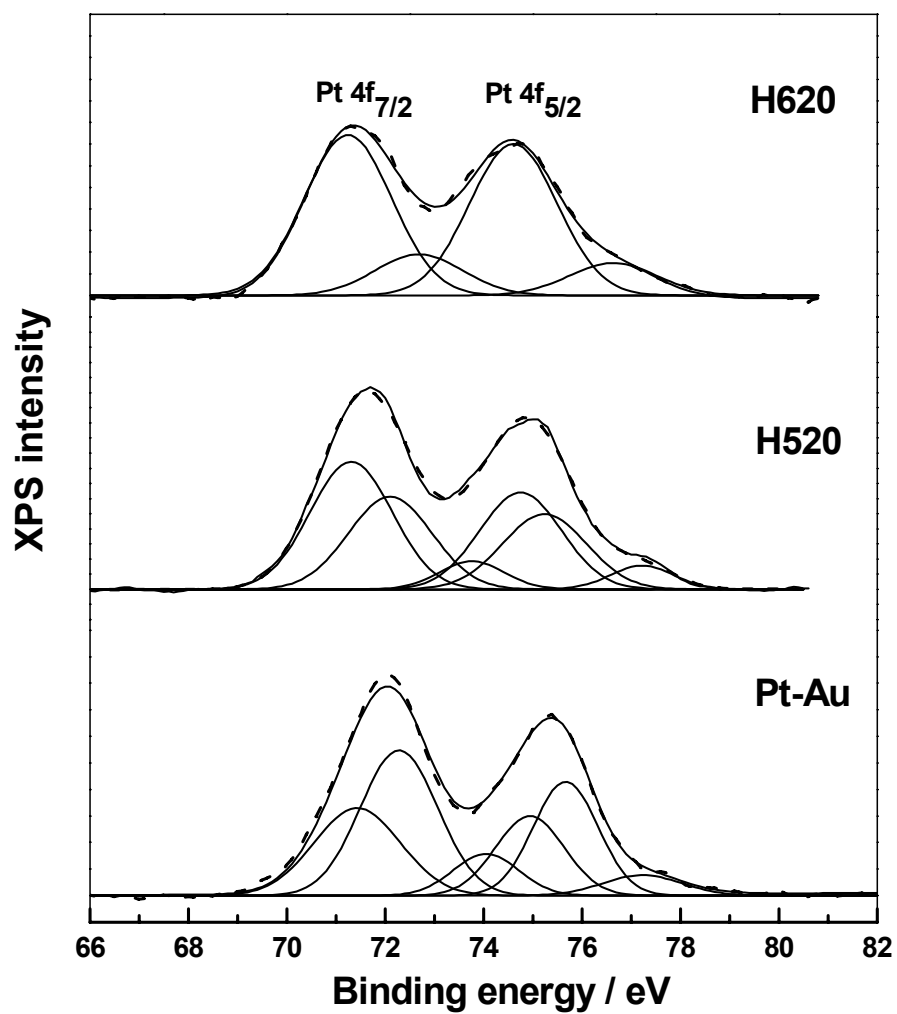


Figure S2† XPS spectra of Pt 4f for the Pt-Au and H₂-treated Pt-Au catalysts.

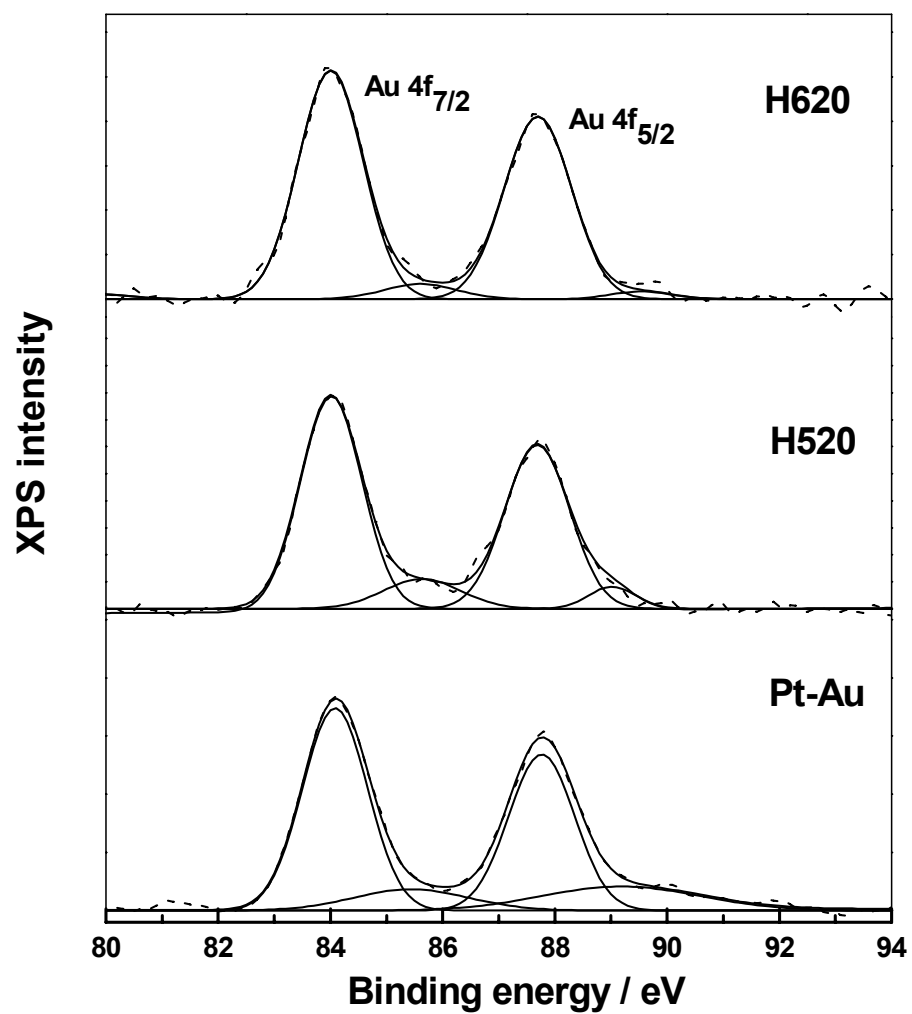


Figure S3† XPS spectra of Au 4f for the Pt-Au and H₂-treated Pt-Au catalysts.

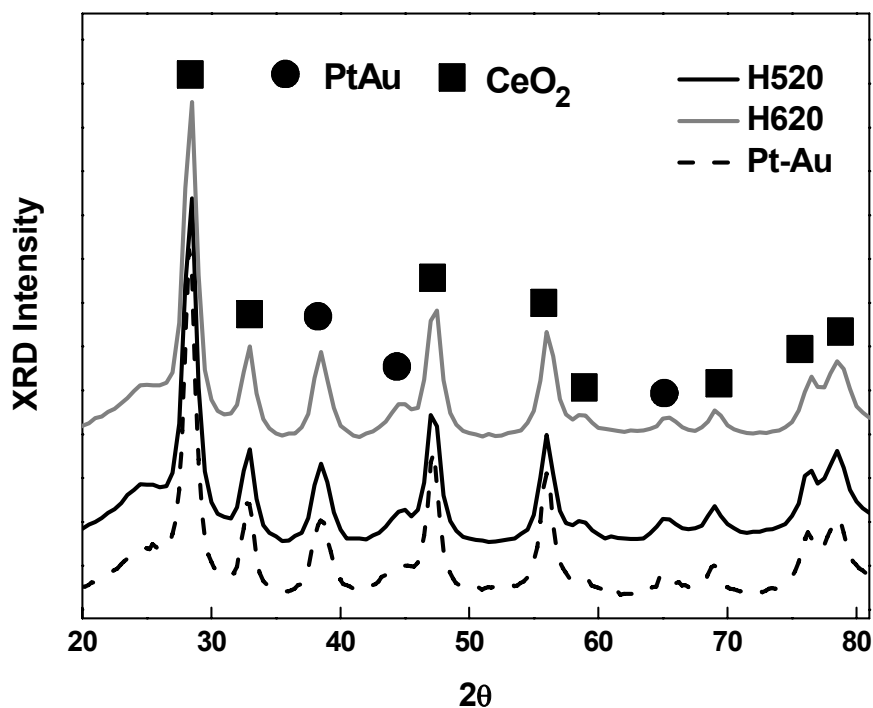


Figure S4† XRD patterns of Pt-Au and H₂-treated Pt-Au catalysts. According to the Scherrer's equation, the CeO₂ has an average size of 7.1 – 8.5 nm for unheated and H₂-treated samples. The crystalline size of Pt-Au alloys deposited on the carbon support for Pt-Au and H620 samples was about 3.8 and 7.0 nm, respectively.

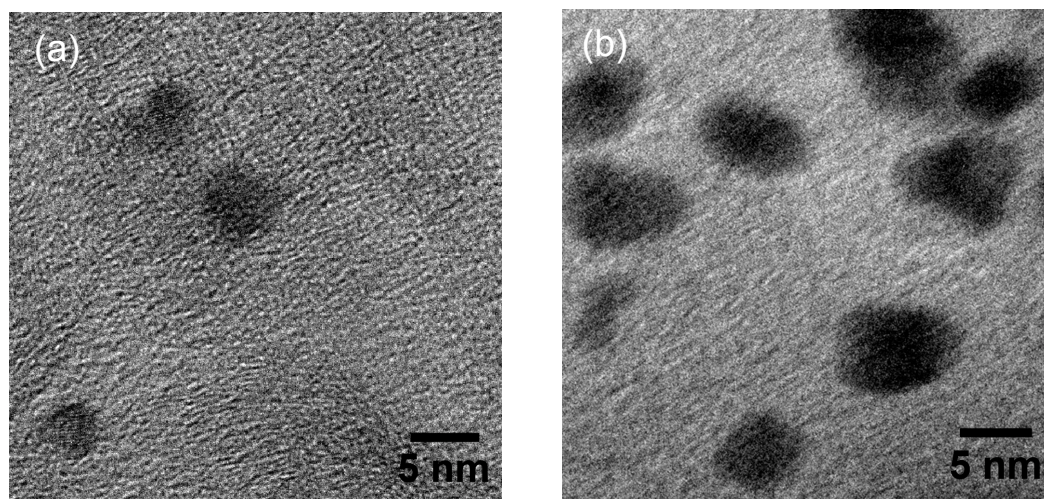


Figure S5† HRTEM images of (a) H520 and (b) H620 catalysts.

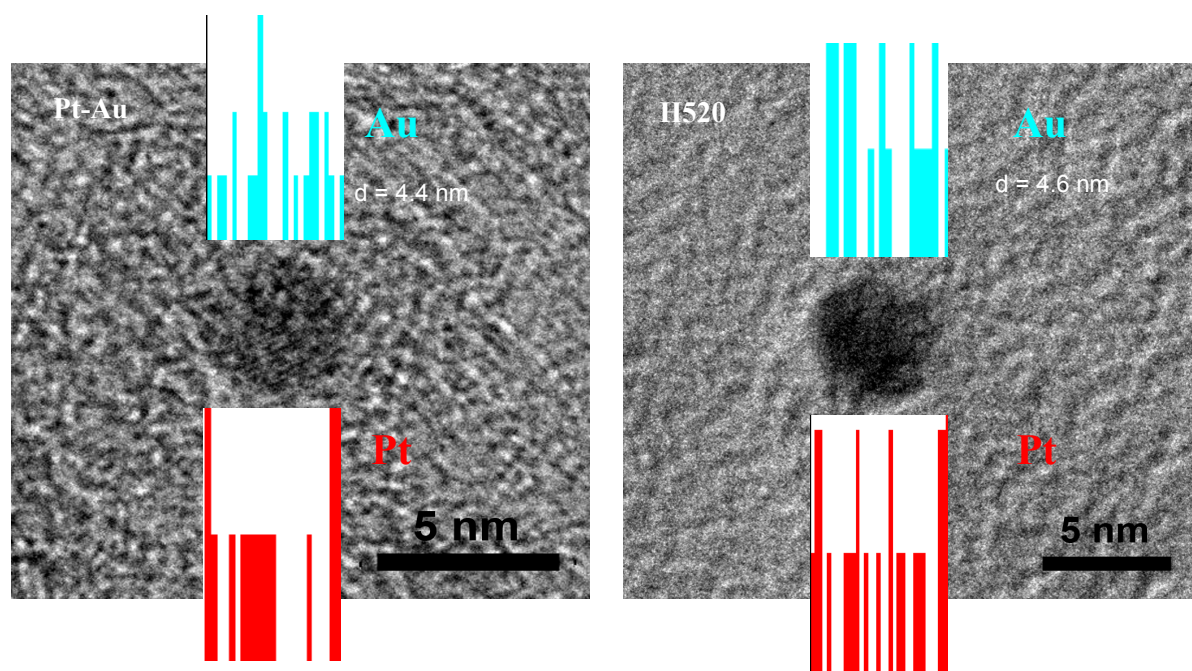


Figure S6† HRTEM images and line scan results of Pt-Au and H520 catalysts in specific nanoparticles.