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Supporting Information for

Precursor-mediated Size Tuning of Monodisperse PtRh Nanocubes as Efficient Electrocatalysts for Ethylene Glycol Oxidation

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1. Experimental section

1.1 Materials and Reagents

Platinum(II) acetylacetonate (Pt(acac)$_2$, 97%), Rhodium(II) acetate (Rh(OAc)$_2$, 40% Rh) and Rhodium (III) chloride trihydrate ($RhCl_3$, 99%) was purchased from Shanghai Macklin Biochemical Co. Ltd. Oleylamine (OAm, 80-90%), 1-octadecene (ODE, 95%), ascorbic acid (AA, 99%) and Tungsten carbonyl ($W(CO)_6$, 98%) were all purchased from Aladdin Co. Ltd. Glucose ($C_6H_{12}O_6$, A.R. grade, 98%), ethanol (CH_3CH_2OH, A.R. grade, 98%), ethylene glycol (EG, A.R. grade, >99.5%), cyclohexane (C_6H_{12}, A.R. grade, 98%) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Water (H_2O, 18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

1.2 Synthesis of Pt nanocubes (Pt NCs)， PtRh-small nanocubes (PtRh-S NCs) and PtRh-large nanocubes (PtRh NCs).

Pt NCs were prepared following a previous report for reference in electrochemical tests [22]. In the typical preparation of PtRh-S NCs, $Pt(acac)_2$ (10 mg), $Rh(OAc)_2$ (1.8 mg), $W(CO)_6$ (5 mg), AA (20 mg), glucose (40 mg), 4 mL OAm and 1 mL ODE were dissolved into a glass vial (volume: 20 mL). After the vial had been capped, the mixture was ultrasonicated for 1.5 h. Subsequently, the resulting homogeneous mixture was then heated from room temperature to 180 °C and maintained at 180 °C for 3 h in an oil bath. The products were collected by centrifugation and washed three times with a cyclohexane/ethanol mixture. The obtained sample was denoted as PtRh-S NCs. The preparations of PtRh-L NCs was similar to the above process by adjusting $RhCl_3$ to 1.3 mg and $W(CO)_6$ to 8 mg, while keeping other reaction conditions same.

1.3 Characterizations

The structure and morphology of samples were investigated by a Hitachi HT7700 transmission electron microscope, which conducted at an acceleration voltage of 120 kV. High resolution TEM (HRTEM), High-Angle Annular Dark-Field Scanning TEM (HAADF-STEM), and corresponding EDS mappings were also obtained on an FEI Tecnai F20 TEM at the same accelerating voltage of 200 kV. The X-ray diffraction (XRD) analysis was carried out on a high resolution X’Pert-Pro MPD diffractometer

(Netherlands PANalytical) equipped with Cu Kα radiation of 1.540598 Å to study the structure and crystal properties of products. Furthermore, the elemental states were analyzed by X-ray photoelectron spectroscopy (XPS), which conducted on a VG Scientific ESCALab 220 XL electron spectrometer with 300 W Al Kα radiation. The energy dispersive X-ray spectrometer (EDS, S-4700, Japan) was operated on an acceleration voltage of 15 kV to analyze the detailed elemental composition of samples.

1.4 Electrochemical measurements

The electrochemical measurements were performed in a three-electrode cell system. The working electrode, counter electrode, and reference electrode were glassy carbon electrode (GCE, diameter: 3.0 mm), platinum wire, saturated calomel electrode (SCE), respectively. To prepare the catalyst-coated working electrode, the catalyst was dispersed in a mixture containing isopropanol and Nafion (5%) to form a 0.40 mg_{Pt}/mL dispersion. 5 μL isopropanol dispersion was deposited on a glassy carbon electrode and dried naturally. The electrochemical active surface area (ECSA) of as-prepared catalysts were corresponding to the surface active sites and could be measured by cyclic voltammetry (CV) in 1 M KOH solution at the scanning rate of 50 mV s^{-1}. EGOR was carried out in 1 M KOH + 1 M EG solution. For durability tests, successive CVs for 250 cycles, and Chronoamperometry (CA) measurements of as-prepared catalysts were also performed. All the electrochemical tests were conducted by electrochemical work station (CHI760E) produced by Chen Hua Instrumental Co. Ltd (Shanghai, China).

2. Supporting figures and tables

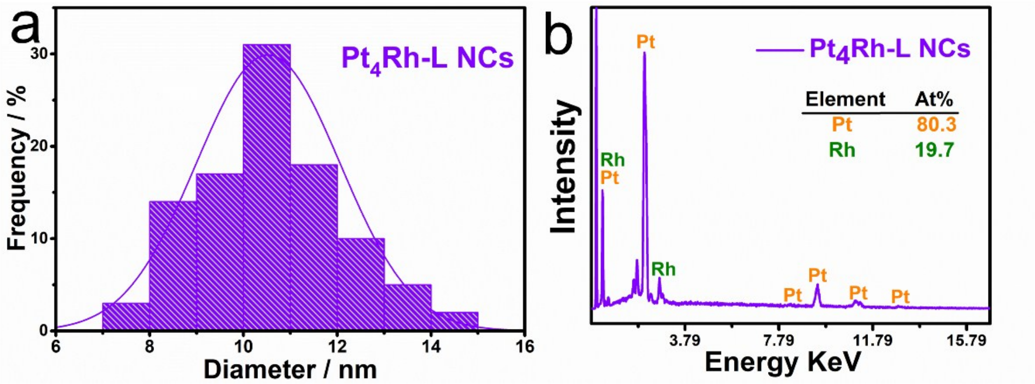

Fig. S1 (a) size distribution and (b) SEM-EDS spectrum of Pt$_4$Rh-L NCs

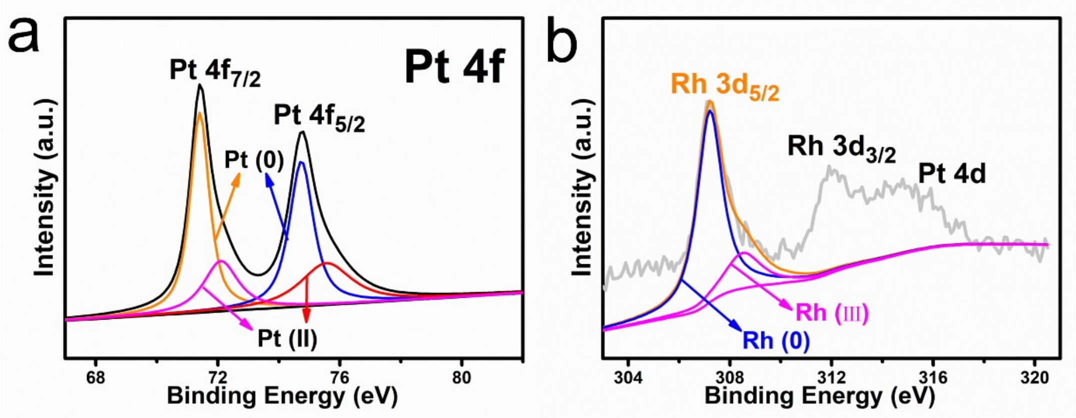

Fig. S2 XPS spectra of (a) Pt 4f, and (b) Rh in Pt$_4$Rh-S NCs.

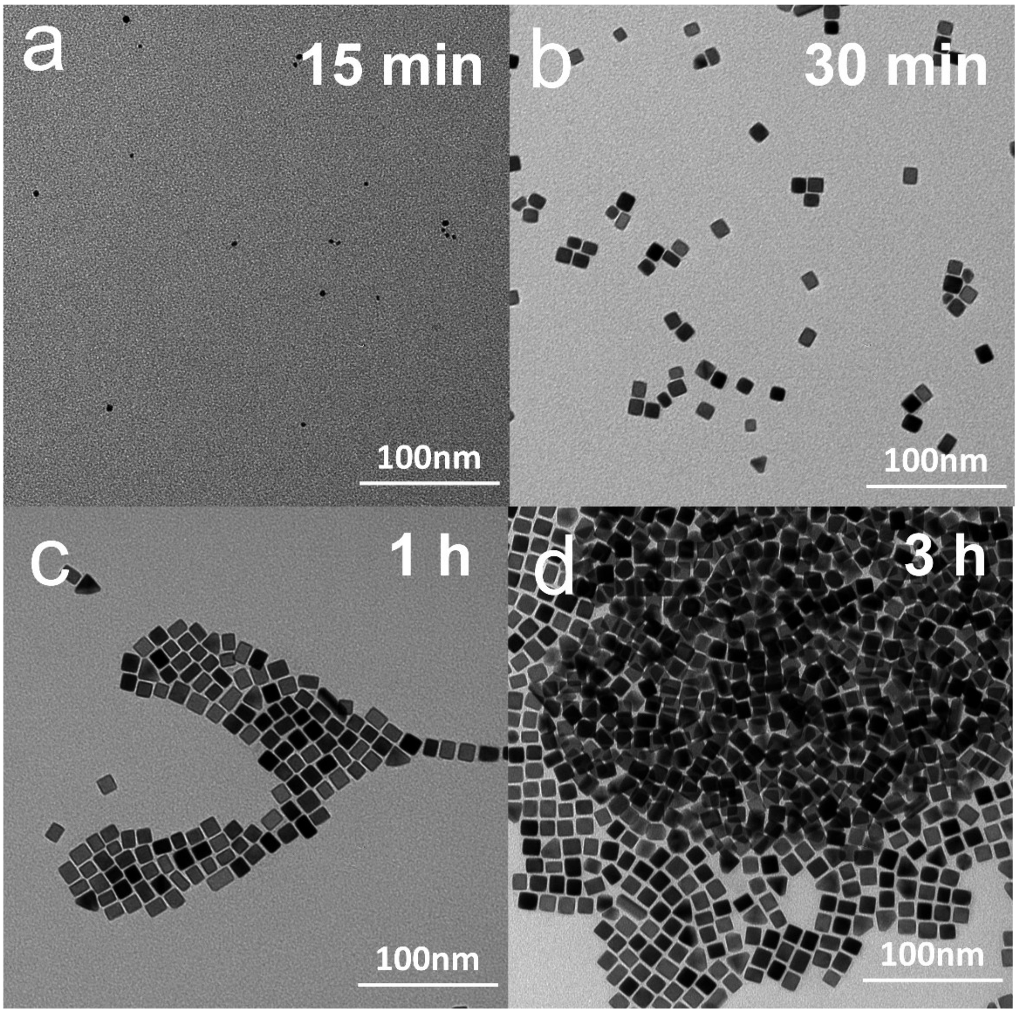

Fig. S3 TEM images of intermediates at (a) 15 min, (b) 30 min, (c) 1 h, and (d) 3 h on the formation process of Pt_4Rh-L NCs catalysts.

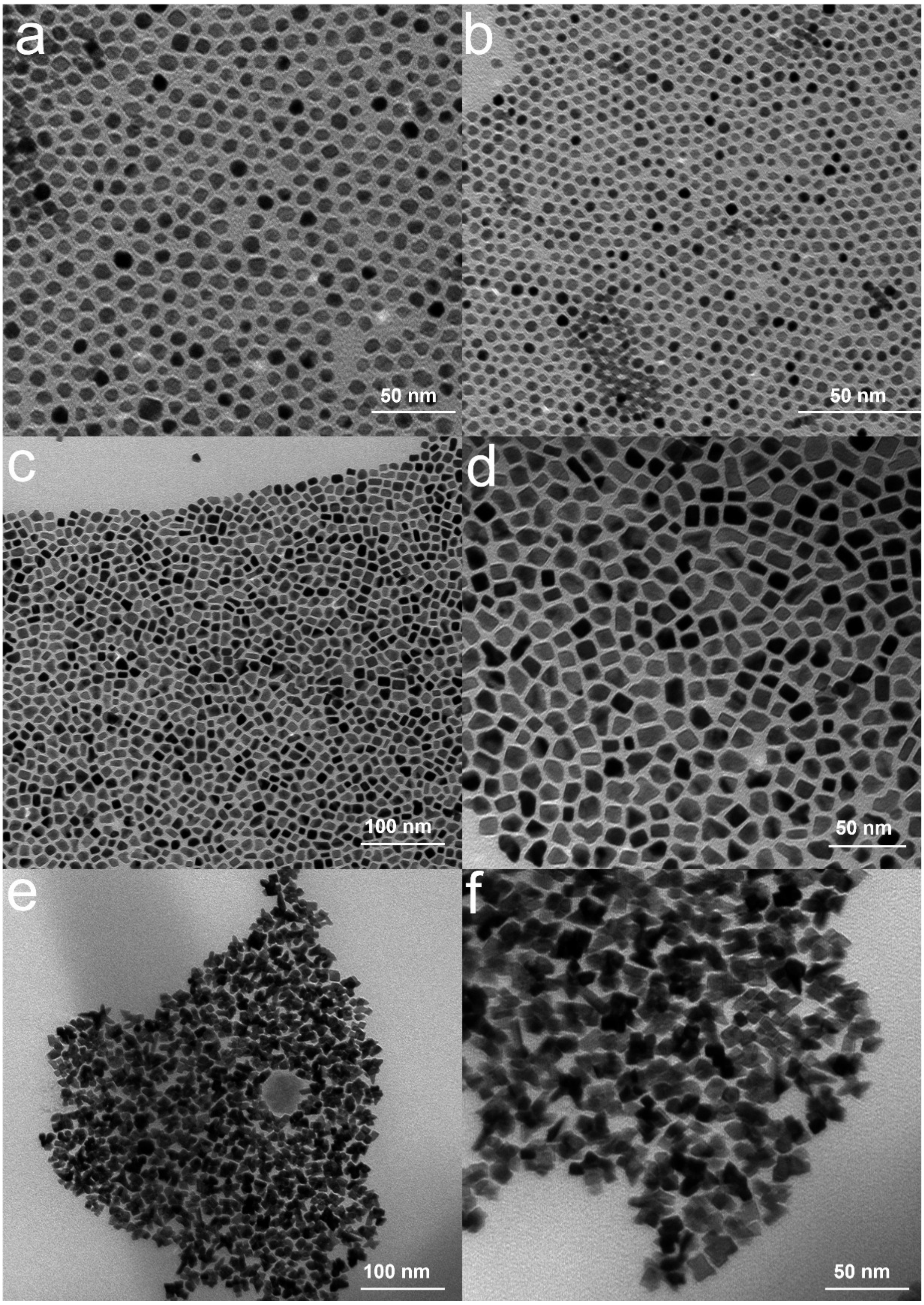

Fig. S4 TEM images of the products with the same reaction conditions as that of Pt_4Rh-L NCs in the absence of (a and b) AA, (c and d) glucose, and (e and f) $W(CO)_6$.

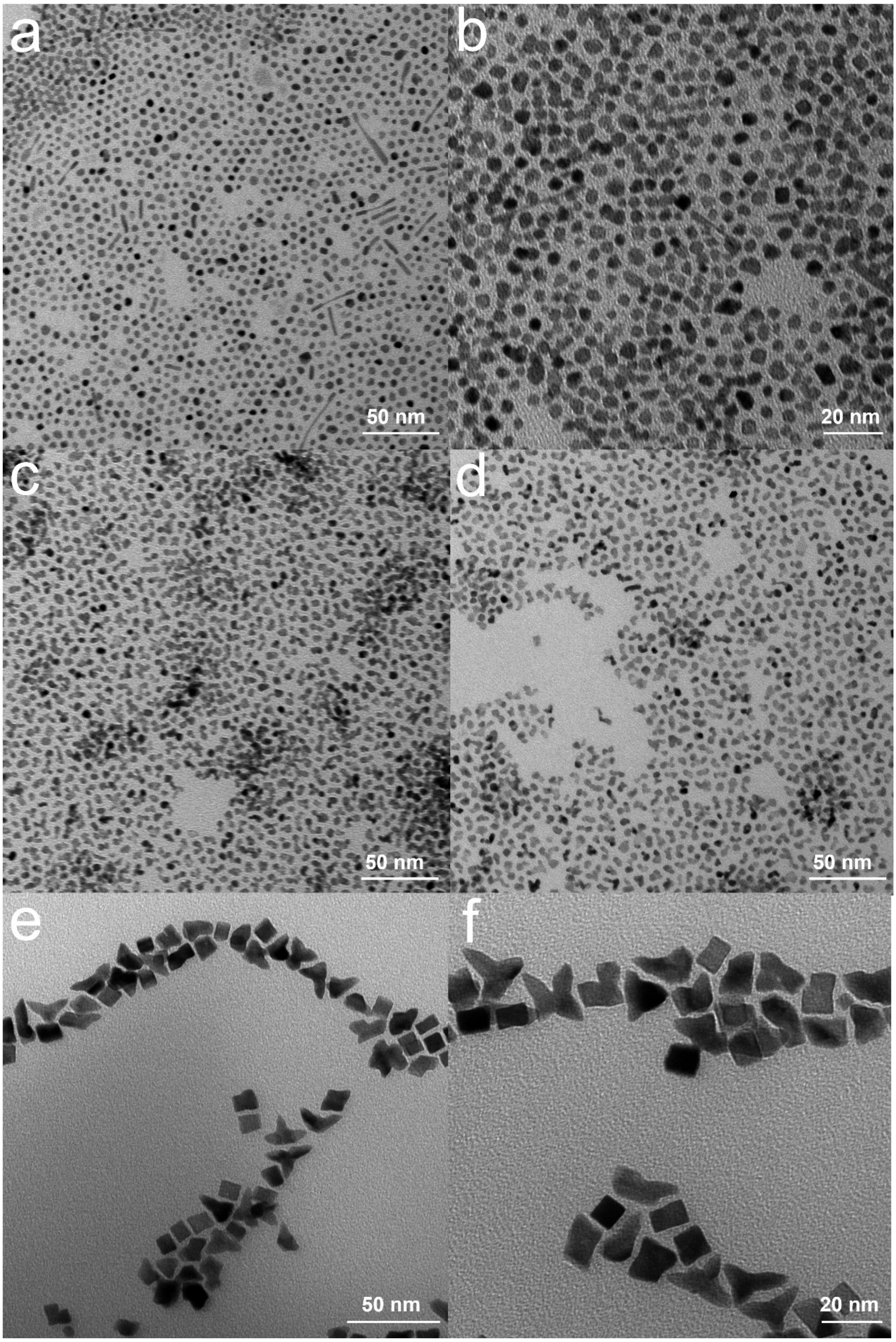

Fig. S5 TEM images of the products with the same reaction conditions as that of Pt_4Rh-S NCs in the absence of (a and b) AA, (c and d) glucose, and (e and f) $W(CO)_6$.

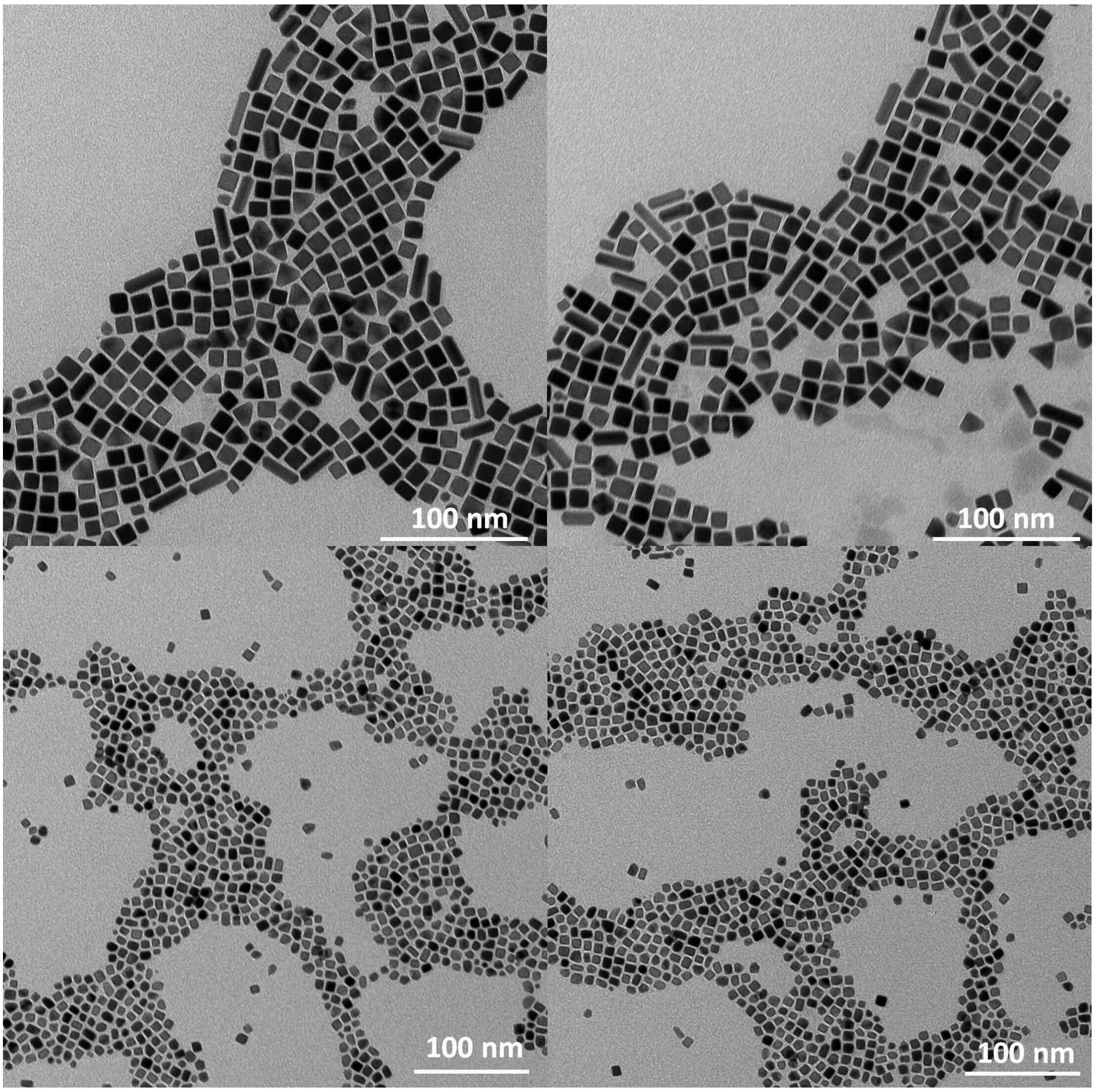

Fig. S6 TEM images of the products with the same reaction conditions as that of (a and b) Pt_4Rh-L NCs and (c and d) Pt_4Rh-S NCs without the addition of ODE.

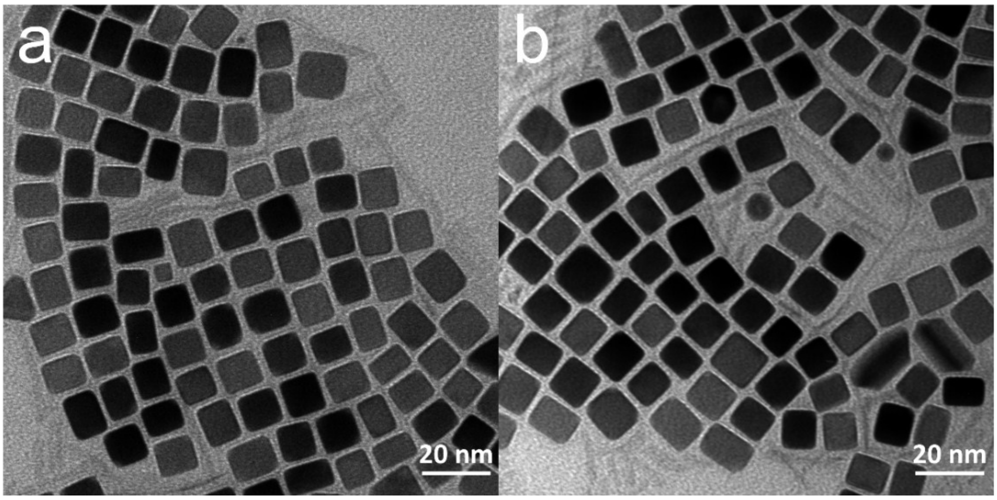

Fig. S7 TEM images of Pt NCs.

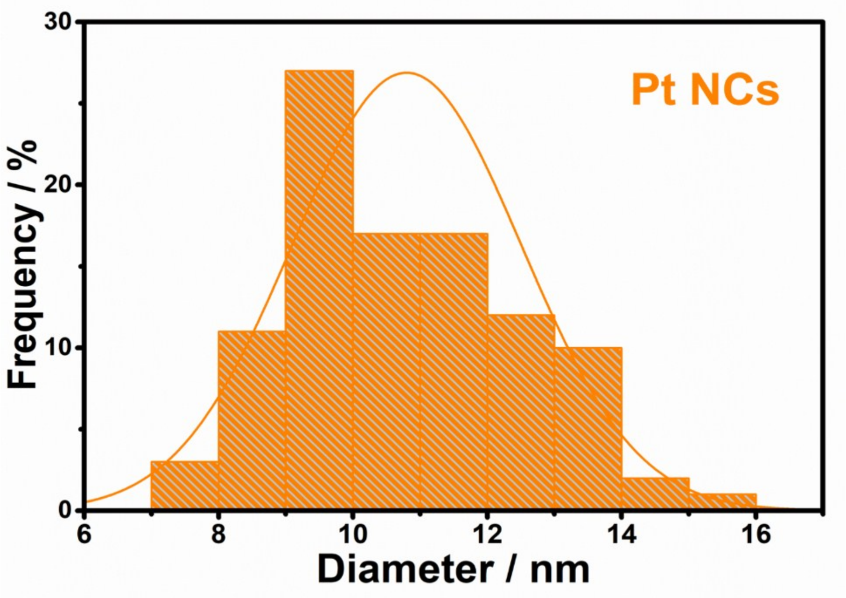

Fig. S8 Size distribution of Pt NCs.

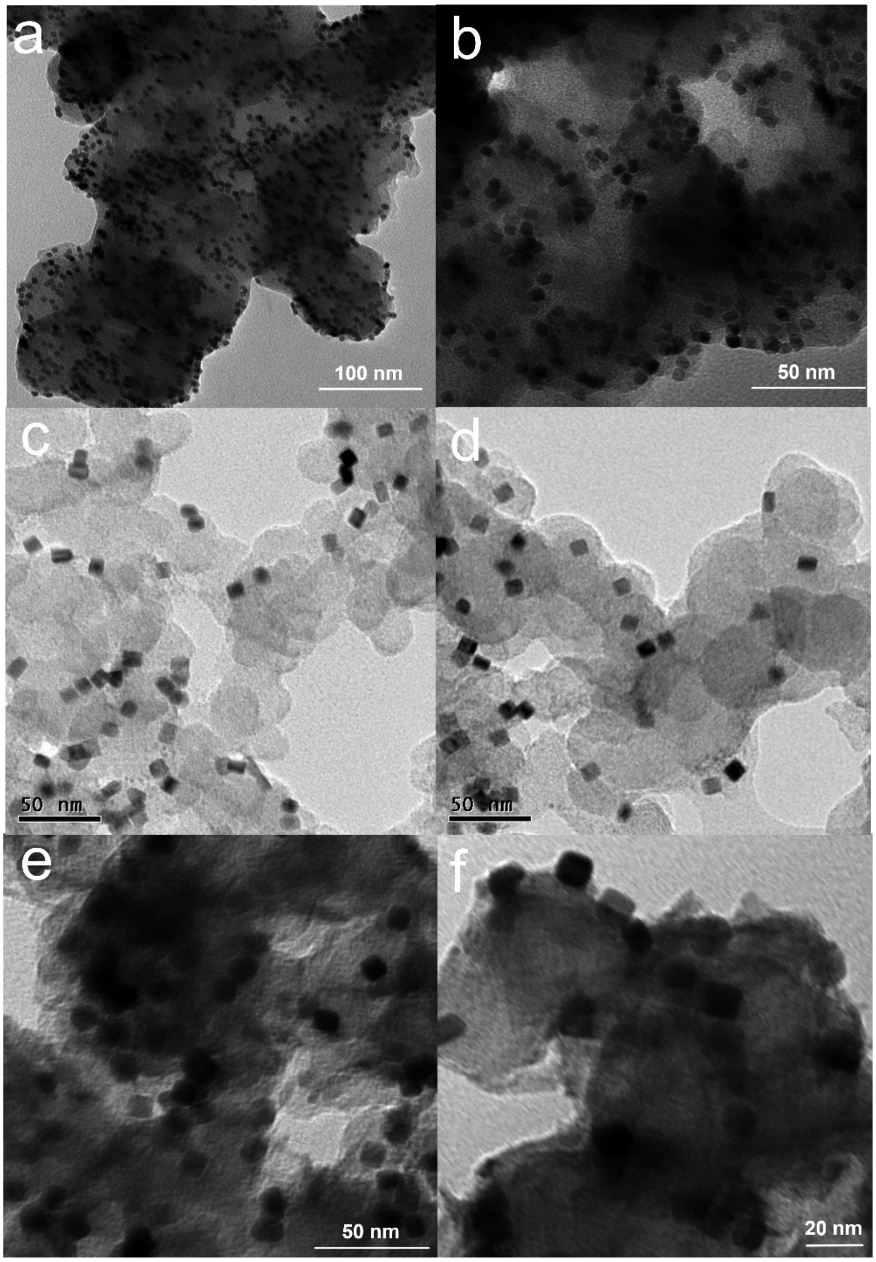

Fig. S9 Representative TEM images of (a and b) Pt_4Rh-S NCs, (c and d) Pt_4Rh-L NCs, and (e and f) Pt NCs catalysts before electrochemical measurements.

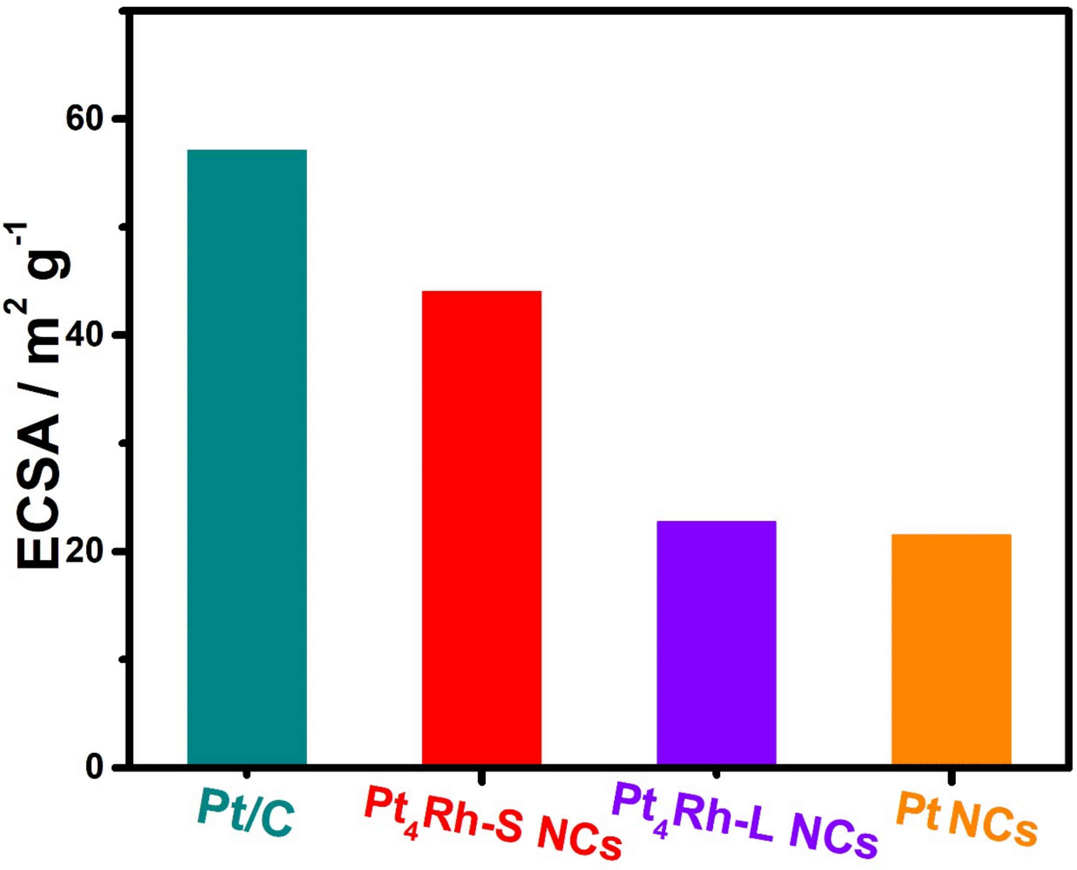

Fig. S10 Calculated ECSA values of different catalysts.

Table. S1 Size of PtRh-S NCs and various PtRh nanocubes from reported literatures.

Catalysts	Size	Reference
Pt_4Rh-S NCs	5.5 nm	This work
Pt_1Rh_1	14.5 nm	*Phys. Chem. Chem. phys : PCCP*, 2014, **16**, 13662-13671.
Cube-shaped dendritic Rh–Pt	36.5 nm	*Nanoscale*, 2015, **7**, 3941-3946.
Pt_1Rh_1/RGO	7.9 nm	*Electrochim. Acta*, 2018, **292**, 208-216.

Table. S2 EGOR performances of PtRh-S NCs and various electrocatalysts from recently reported literatures.

Catalysts	Electrolyte	Mass activity (mA mg^{-1})	Retaned mass activity (mA mg^{-1})	Reference
Pt_4Rh-S NCs	1 M KOH + 1 M EG	5125.0	1356.5	This work
PtAg-s NPs	1 M KOH +1 M EG	3200	670	*Inorg. Chem. Front.* **2018**, *5*, 1174–1179
$Pt_{31}Cu_{69}$ H TNC	1 M KOH +1 M EG	4406.1	211.6	*Nanoscale,* **2018**, *10*, 8246-8252
Pt_1Ag_1	1 M KOH + 1 M EG	5042.9	1160.4	*Int. J. Hydrogen Energy* **2018**, *43*, 9644-9651
PtRu alloy	1 M KOH + 1 M EG	3052.8	219.5	*Int. J. Hydrogen Energy* **2017**, *42*, 20720-20728.
PtPd@Pt NCs/rGO	0.5 M KOH + 0.5 M EG	1167	89	*Electrochim. Acta* **2016**, *187*, 576-83.
Pt_1Cu_1	1 M KOH + 1 M EG	4259.2	321.1	*Int. J. Hydrogen Energy* **2017**, *43* 1489-1496.