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Surface Ligands-Mediated Isolated Growth of Pt on Pd Nanocube For enhanced Hydrogen Evolution Activity

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1.Materials and Methods

Materials

Ethylene glycol (EG), L-ascorbic acid (AA) and potassium bromide (KBr) were obtained from Beijing Chemical Reagents, China. Sodium tetrachloropalladate(II) tetrachloride (Na_2PdCl_4, 99%), were acquired from Sigma-Aldrich. $Pt(acac)_2$ (99%), $Cu(acac)_2$ (99%) and PVP (MW=5,5000, AR) were purchased from Alfa Aesar. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ·cm.

Experimental Section

Synthesis of Pd Nanocubes,[1] The Pdnanocubes used as seeds for the synthesis of Pd-Pt bimetallic nanocrystals were synthesized by adding a Na_2PdCl_4 solution into a mixture of PVP,AA and KBr. Typically, PVP (105 mg), AA (60 mg), and KBr (600 mg) were dissolved in DI water (8.0 mL), and then placed in a vial and pre-heated at 80 °C in an oil bath under magnetic stirring for 10 min. Subsequently, Na_2PdCl_4 (57 mg) was dissolved in DI water (3.0 mL) and then injected into the preheating solution. The mixture of reagents was capped, and maintained at 80 °C for 3 h. The product was collected by centrifugations, washed three times with water to remove excess PVP and inorganic ions, and then re-dispersed in EG (10 mL).

Synthesis of Pd@L-Pt, The layered growth mode core-shell structures were synthesized through seed-induced growth methods. In a standard synthesis, L-ascorbic acid (53 mg), 18-nm Pd nanocubes solution in EG(1.0 mL), and EG (6.0 mL) were mixed together in a 25-mL flask. The mixture was pre-heated at 140°C under magnetic stirring. Meanwhile, $Pt(acac)_2$ (15.3 mg) and PVP (100 mg) were dissolved in EG (6.0 mL). Then, the EG solution was pumped into the pre-heated mixture held at 140 °C at the rate of 0.4 mL/min. The reaction was allowed to continue for an additional 1 hour to complete. The product was collected by centrifugation, washed twice with ethanol and three times with water, and then re-dispersed in ethanol (1mL).

Synthesis of Pd@I-Pt, The island growth mode core-shell structures were synthesized used the same approach. In a standard synthesis, L-ascorbic acid (53 mg), KBr (54 mg), 18-nm Pd nanocubes solution in EG (1.0 mL), and EG (6.0 mL) were mixed together in a 25-mL flask. The mixture was pre-heated at 140 °C under magnetic stirring. Meanwhile, $Pt(acac)_2$ (15.3 mg) and PVP (100 mg) were dissolved in EG (6.0 mL). Then, the EG solution was pumped into the pre-heated mixture held at 140°C at the rate of 0.4 mL/min. The reaction was allowed to continue for an additional 1 hour to complete. The product was collected by centrifugation, washed twice with ethanol and three times with water, and then re-dispersed in ethanol (1mL).

Synthesis of Pd@L-PtCu, In a standard synthesis, L-ascorbic acid (53 mg), 18-nm Pd nanocubes solution in EG(1.0 mL), and EG (6.0 mL) were mixed together in a 25-mL flask. The mixture was pre-heated at 140°C under magnetic stirring. Meanwhile, Pt(acac)$_2$ (15.3 mg), Cu(acac)$_2$ (10.2 mg) and PVP (100 mg) were dissolved in EG (6.0 mL). Then, the EG solution was pumped into the pre-heated mixture held at 140 °C at the rate of 0.4 mL/min. The reaction was allowed to continue for an additional 1 hour to complete. The product was collected by centrifugation, washed twice with ethanol and three times with water, and then re-dispersed in ethanol (1mL).

Synthesis of Pd@I-PtCu and Pd@I-PtCu$_3$, L-ascorbic acid (53 mg), KBr (54 mg), 18-nm Pd nanocubes solution in EG (1.0 mL), and EG (6.0 mL) were mixed together in a 25-mL flask. The mixture was pre-heated at 140°C under magnetic stirring. Meanwhile, Pt(acac)$_2$ (15.3 mg), Cu(acac)$_2$ (10.2 mg for Pd@PtCu and 30.6 mg for Pd@PtCu$_3$) and PVP (100 mg) were dissolved in EG (6.0 mL). Then, the EG solution was pumped into the pre-heated mixture held at 140°C at the rate of 0.4 mL/min. The reaction was allowed to continue for an additional 1 hour to complete. The product was collected by centrifugation, washed twice with ethanol and three times with water, and then re-dispersed in ethanol (1mL).

Electrochemical measurements

Electrochemical measurements were performed using a glassy carbon rotating disk electrode. A leak-free AgCl/Ag/KCl (3M) electrode was used as the reference. All potentials were converted to values with reference to a reversible hydrogen electrode (RHE). The counter electrode was a platinum wire. The electrolyte was 0.5 M H_2SO_4.

Preparation of working electrode

For the catalyst supported on Vulcan XC-72 carbon (20wt% of Pt and 5% Nafion solution) was prepared to an ethanol solution of 4mg/mL(based on ICP-MS measurement), and sonicated for 30 min. 8 microliters of the dispersion was then transferred onto the glassy carbon RDE with a geometric area of 0.196cm^2. Drying in air for 30 minutes before measurement.

Hydrogen evolution reaction (HER)

The HER measurements were performed in 0.5 M H_2SO_4 solutions under flow of N_2 using the glassy carbon RDE at a rotation rate of 1,600 rpm and a sweep rate of 50 mV/s. In order to produce a clean electrode surface, 60 potential sweeps between -0.05 and 1.3 V versus RHE were applied to the electrode prior to the HER measurement. In the HER polarization curve, current densities were normalized in reference to the geometric area of the glassy carbon RDE (0.196 cm^2).

2. Figures and Schemes

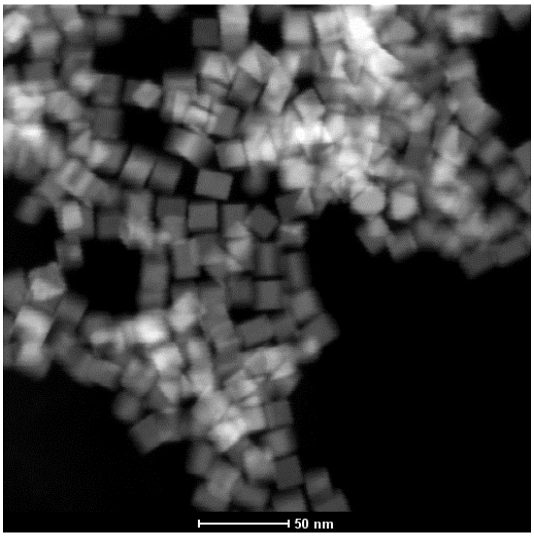

Figure S1: HAADF-STEM image of layered growth mode Pd@L-Pt

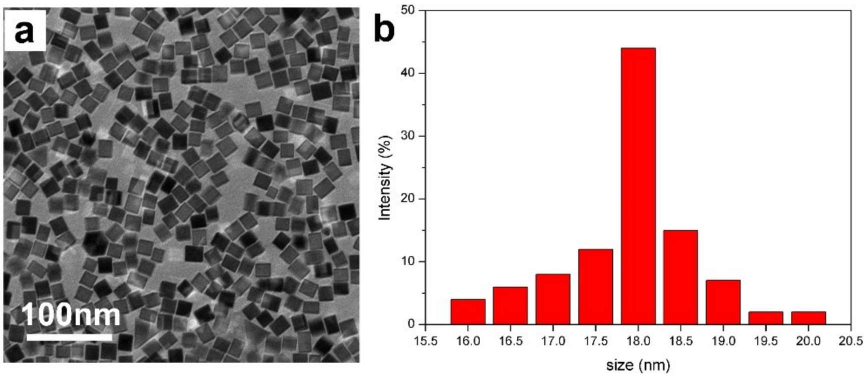

Figure S2: (a) TEM image of Pd nanocubes and (b) their diameter and intensity ratio distribution. The average diameter is 18nm ± 2nm, by measuring 100 particles.

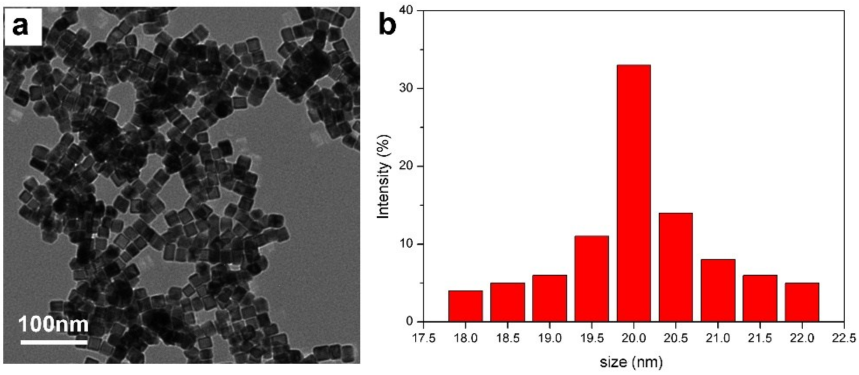

Figure S3: (a) TEM image of layered growth mode Pd@L-Pt and (b) their diameter and intensity ratio distribution. The average diameter is 20nm ± 2nm, by measuring 100 particles.

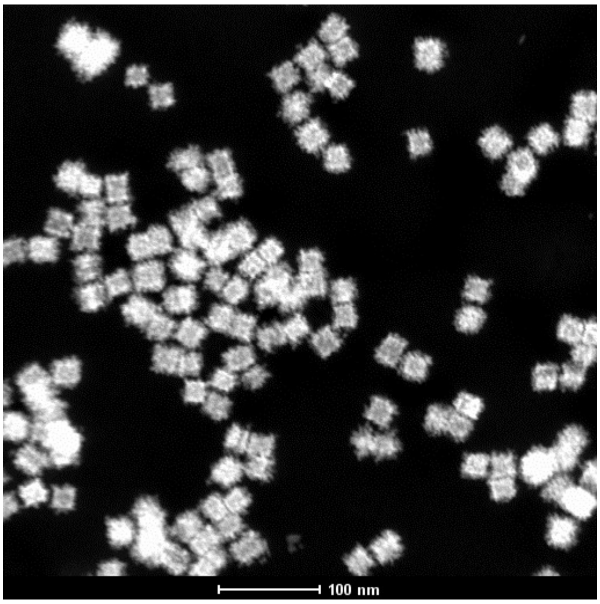

Figure S4: HAADF-STEM image of island growth mode Pd@I-Pt

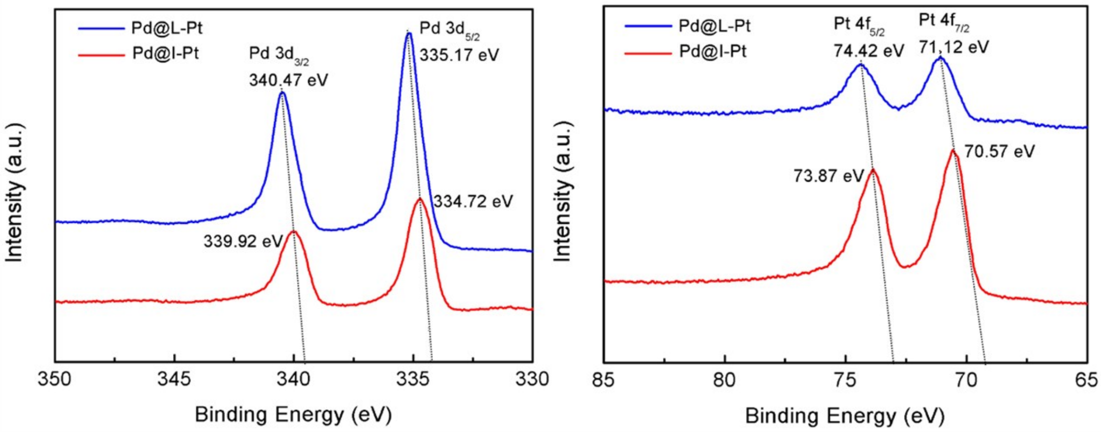

Figure S5 : XPS spectra of Pd 3d (left) and Pt 4f (right) for Pd @ L-Pt and Pd @ I-Pt.

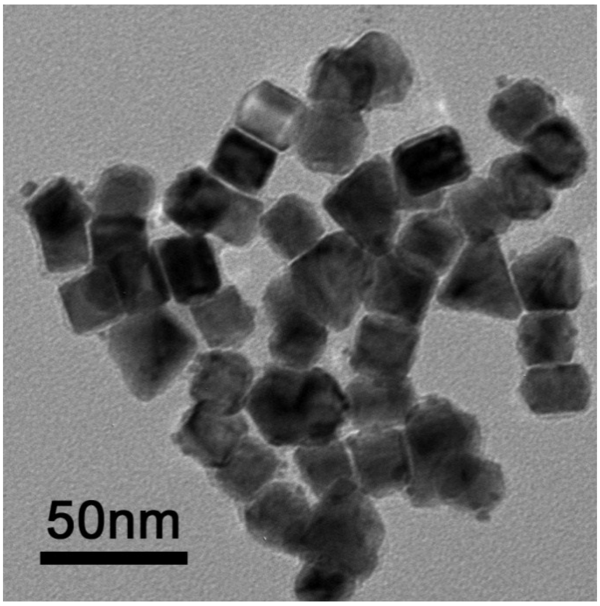

Figure S6: TEM image of Layered growth mode Pd@L-PtCu

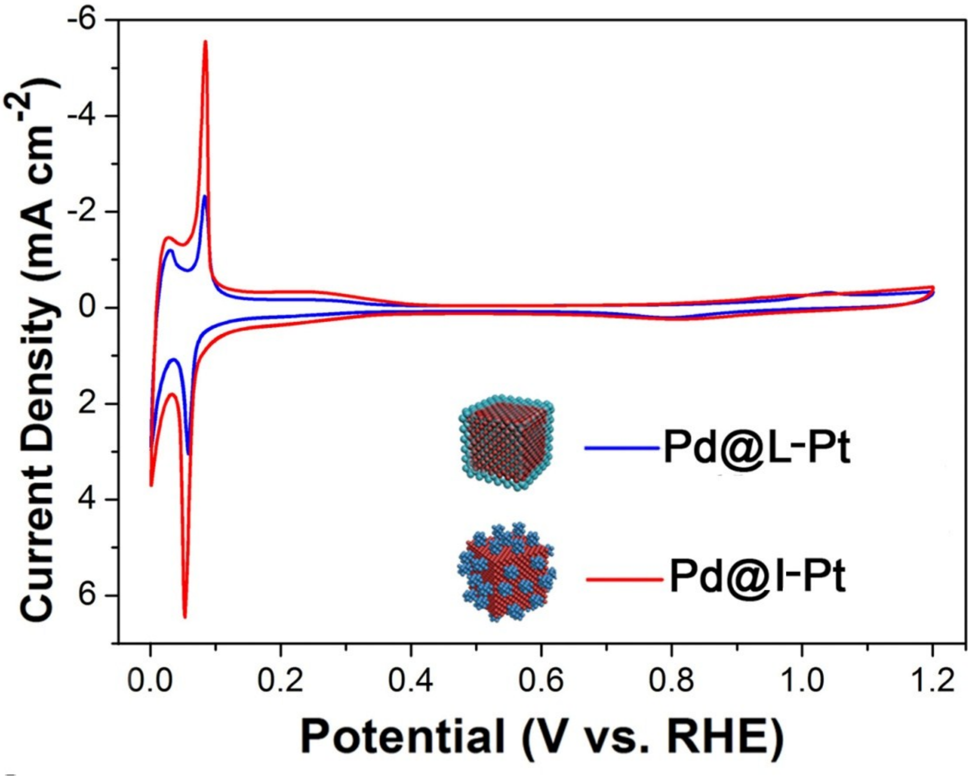

Figure S7: CV curves for the Pd@Pt with layered growth mode and island growth mode. The calculated ECSA for Pd@L-Pt is 33.8cm^2/mg and for Pd@I-Pt is 127cm^2/mg.

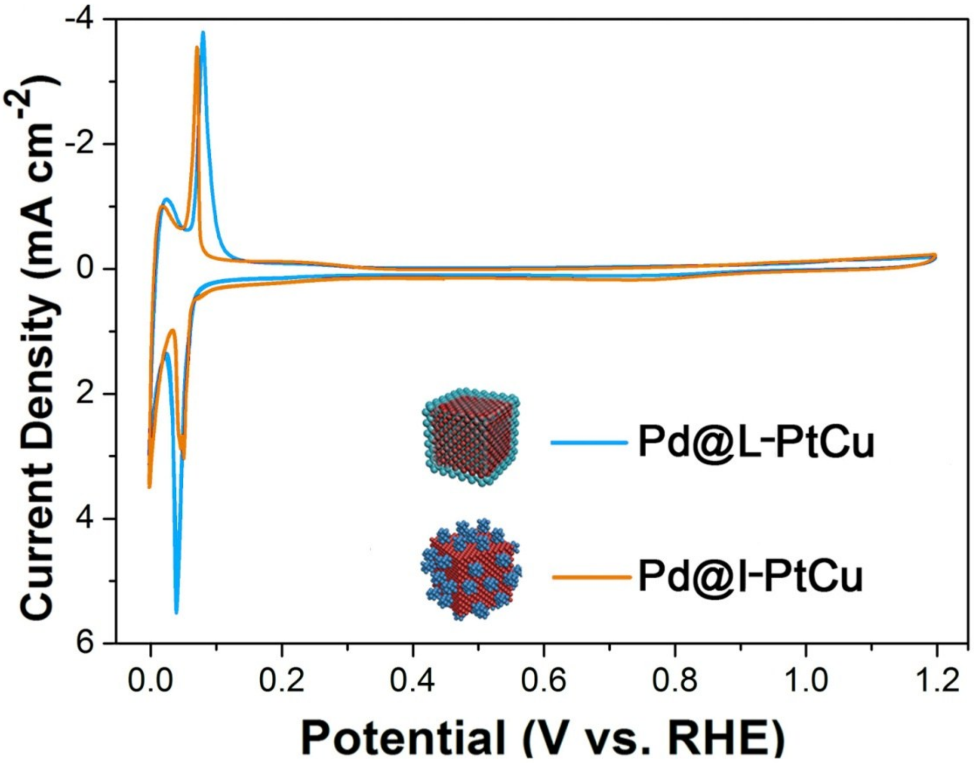

Figure S8: CV curves for the Pd@PtCu with layered growth mode and island growth mode

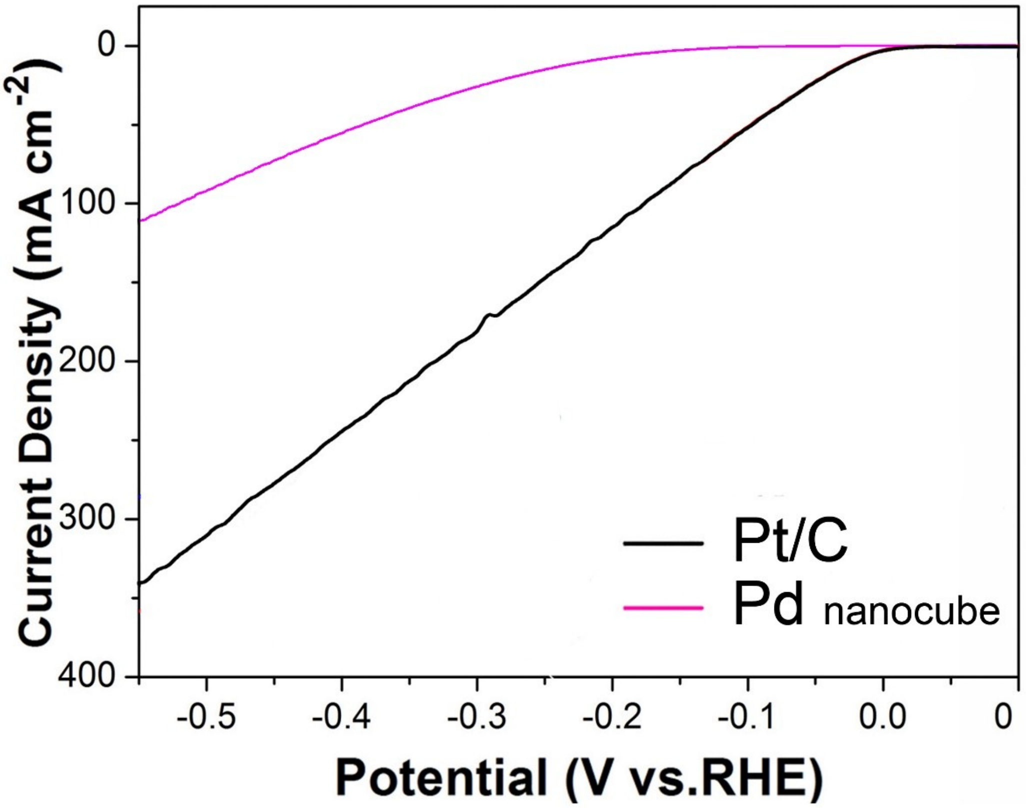

Figure S9: HER electrocatalytic properties of Pd nanocube and Pt/C

Table S1: ICP-MS datas of Pd@PtCu and Pd@$PtCu_3$

entry	Precursor molar ratios （Pt-Cu）	Analyzed Pt molarity μg/mL	Analyzed Cu molarity μg/mL
1	1:1	110.1	32.35
2	1:3	258.48	226.8

References

1. H. Zhang, M. Jin, H. Liu, J. Wang, M. J. Kim, D. Yang, Z. Xie, J. Liu and Y. Xia, *ACS nano*, 2011, **5**, 8212-8222.