

## Electronic Supplementary Information

### Highly stable and efficient Pd<sub>6</sub>(SR)<sub>12</sub> cluster catalyst for hydrogen and oxygen evolution reactions

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#### Experimental Section

**Chemicals and materials:** Palladium chloride (PdCl<sub>2</sub>, Beijing Chemical Works), tetraoctylammonium bromide (TOABr, 98%, Aldrich), 1-dodecanthiol (98%, Alfa Aesar), sodium tetrahydroborate (NaBH<sub>4</sub>, 98%, powder, ACROS). Methanol (AR), dichloromethane (AR) and tetrahydrofuran (THF, AR) were obtained from the Beijing Chemical Works.

**Characterizations and instruments.** UV-Vis spectra were performed on a UV-3000PC Spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). X-ray photoelectron energy spectra were obtained from the AVG Thermo ESCALAB 250 spectrometer (VG scientific) operated at 120 W. Fourier-transformed infrared spectroscopy (FTIR) experiments were carried out with a VERTTEX 70 FTIR (KBr wafer technique). Matrix-assisted laser desorption ionization time of flight mass spectra (MALDI-TOF MS) were conducted on the Bruker autoflexIII smartbeam (Germany) and Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene] malononitrile (DCTB) was used as the matrix. Inductively coupled plasma mass spectroscopy (ICP-MS) for determining the amount of Pd was completed by the Thermo Scientific Xseries 2. High-resolution transmission electron microscopy images were acquired from the JEM-2010 (HR) microscope operated at 200 kV. Powder X-ray diffraction (XRD) was operated on the D8 ADVANCE (Germany) using Cu K $\alpha$  radiation with a Ni filter ( $\lambda = 0.154059$  nm at 30 kV and 15 mA).

**Synthesis of the Pd<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>S)<sub>12</sub>.** The synthesis of Pd<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>S)<sub>12</sub> was conducted by following the previous report for Ni clusters with a minor modification.<sup>1</sup> Typically, PdCl<sub>2</sub> (37 mg, 0.21 mmol) was first dissolved into 12.5 ml THF containing 0.32 g TOABr. Then the reaction mixture was

cooled in the ice bath for 30 min before 1-dodecanthiol (300  $\mu$ l) was introduced into the flask under constant stirring. After three hours, the NaBH<sub>4</sub> aqueous solution (0.08 g NaBH<sub>4</sub> dissolved in 2.5 ml ice water) was poured into the reaction mixture under vigorous stirring. The reaction was allowed to react for another three hours at room temperature. The product was obtained after removing THF with rotary evaporation, washed with methanol and extracted with DCM (some insoluble solid was discarded by the centrifugation).

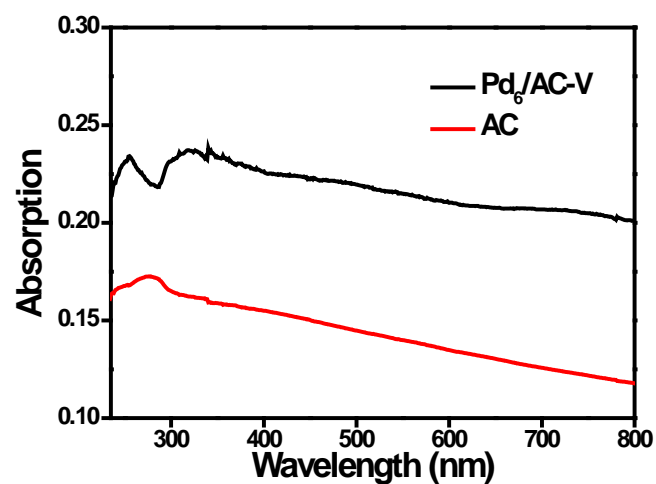
**Synthesis of the Pd<sub>6</sub>/AC.** The DCM solution of Pd<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>S)<sub>12</sub> (5 ml) was mixed with activated carbon (10 mg) in 5 ml DCM under vigorous stirring. Twenty-four hours later, the Pd<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>S)<sub>12</sub> supported on activated carbon (Pd<sub>6</sub>/AC) was collected through vacuum filtration and then dried in vacuum oven at room temperature.

**Synthesis of the Pd<sub>6</sub>/AC-V.** To obtain the ligand-free product, the above dried Pd<sub>6</sub>/AC solid was calcinated under the vacuum atmosphere at the temperature of 200 °C. Note that the slight lower calcination temperature was chosen to lower the loss speed of protecting ligands so that aggregation of metal cores can be avoided. The final product was denoted as Pd<sub>6</sub>/AC-V and its electrocatalytic performances were compared to those of the parent Pd<sub>6</sub>/AC.

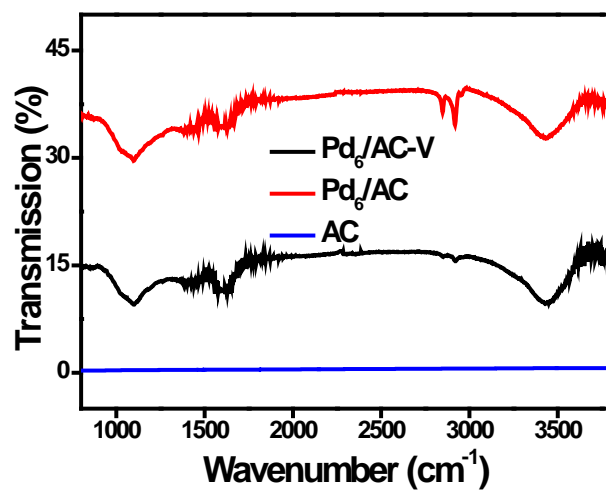
**Electrochemical measurements.** All electrochemical measurements were performed on the CHI 750D electrochemical workstation with a standard three-electrode cell at room temperature. Ag/AgCl was used as reference electrode and Pt coil was used as counter electrode. The working electrodes were prepared by decorating rotating ring disk electrode (geometric area = 0.247 cm<sup>2</sup>) with an amount of catalyst ink containing catalyst (Pd<sub>6</sub>/AC, Pd<sub>6</sub>/AC-V or Pt/C), water, isopropanol and Nafion (water: isopropanol: Nafion = 4:1:0.025). Here, all the recorded currents were given without any iR drop correction during the measurements. For the hydrogen evolution reaction and oxygen evolution reaction, 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M KOH were used as electrolyte, respectively. Linear sweep voltammetry with a scan rate of 5 mV s<sup>-1</sup> was measured to evaluate the catalytic activities of the prepared catalysts. To compare the activities (mass or specific activities) of the prepared samples with those of the commercial Pt/C, the obtained electrochemical currents are normalized to the mass loading of metals (Pt or Pd, obtained from the ICP-MS measurements) or the geometric area of electrode.

Cyclic voltammetry was conducted to investigate the electrochemical stability of the samples. Accelerated durability tests (ADTs) were performed with a potential window from 0.2 to -0.5 V

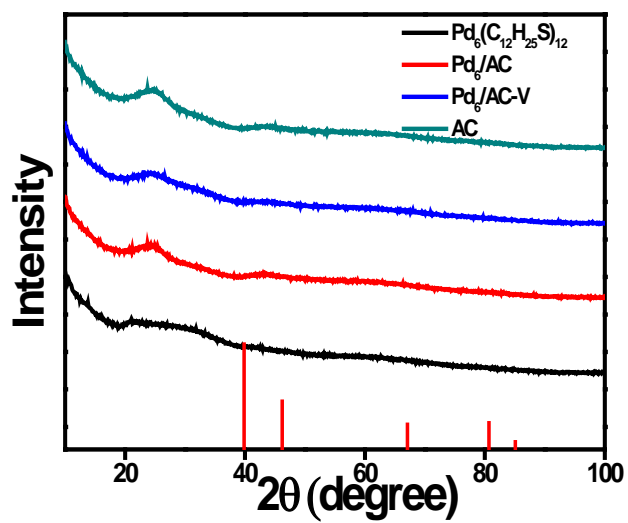
and a scan rate of  $0.1 \text{ V s}^{-1}$  for hydrogen evolution reaction. For oxygen evolution reaction, the ADTs were carried out with a potential range from 1.0 to 1.9 V and a scan rate of  $0.1 \text{ V s}^{-1}$ . In this work, all the potentials versus Ag/AgCl have been converted to a reversible hydrogen electrode (RHE) scale according to the following equation:  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197$ .



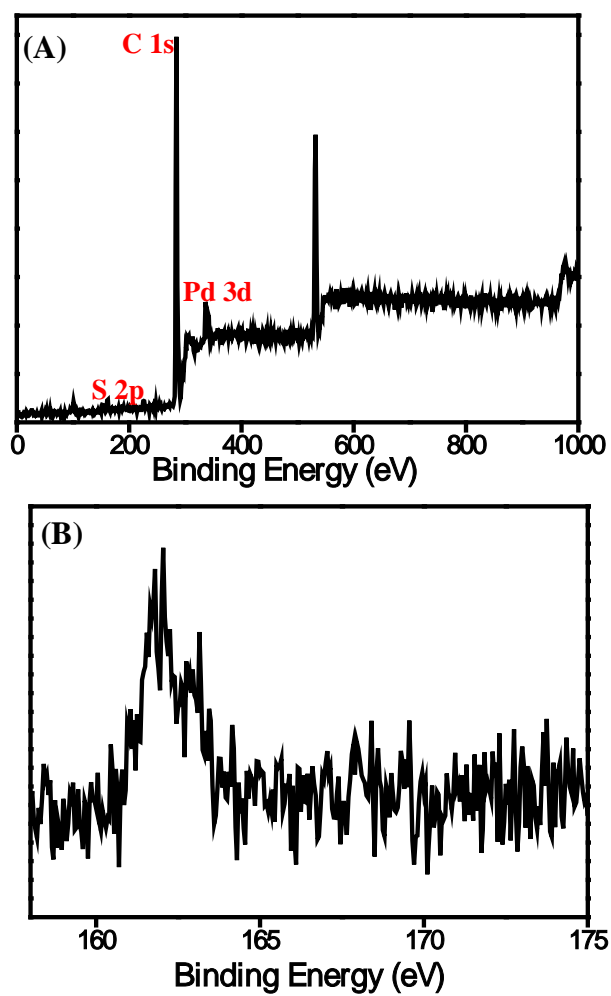
**Fig. S1** UV-Vis absorption spectra of the Pd<sub>6</sub>/AC-V (black line) and the activated carbon (red line).



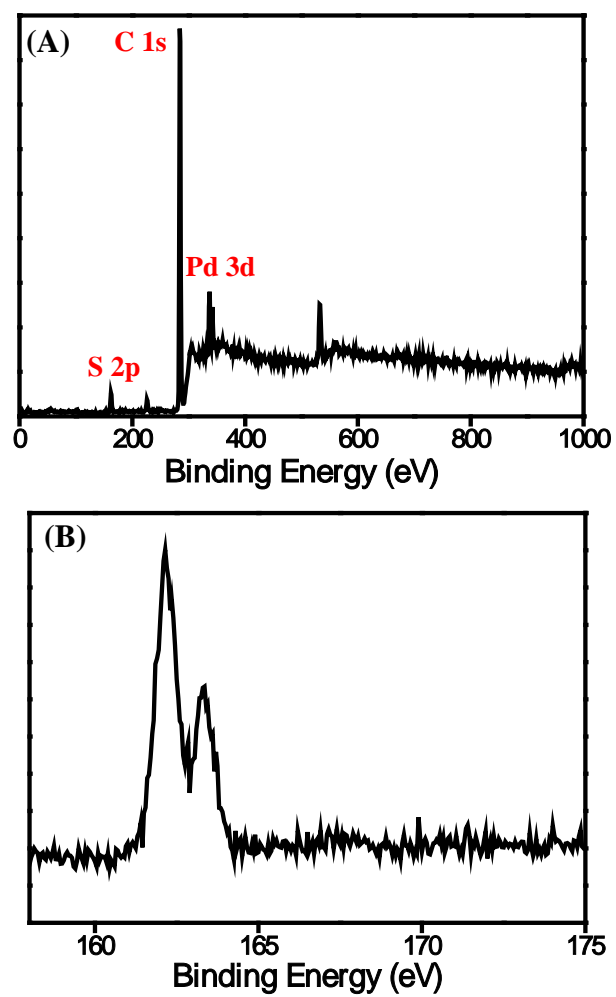
**Fig. S2** Infrared spectra of the Pd<sub>6</sub>/AC (red line), Pd<sub>6</sub>/AC-V (black line) and activated carbon (AC, blue line.)



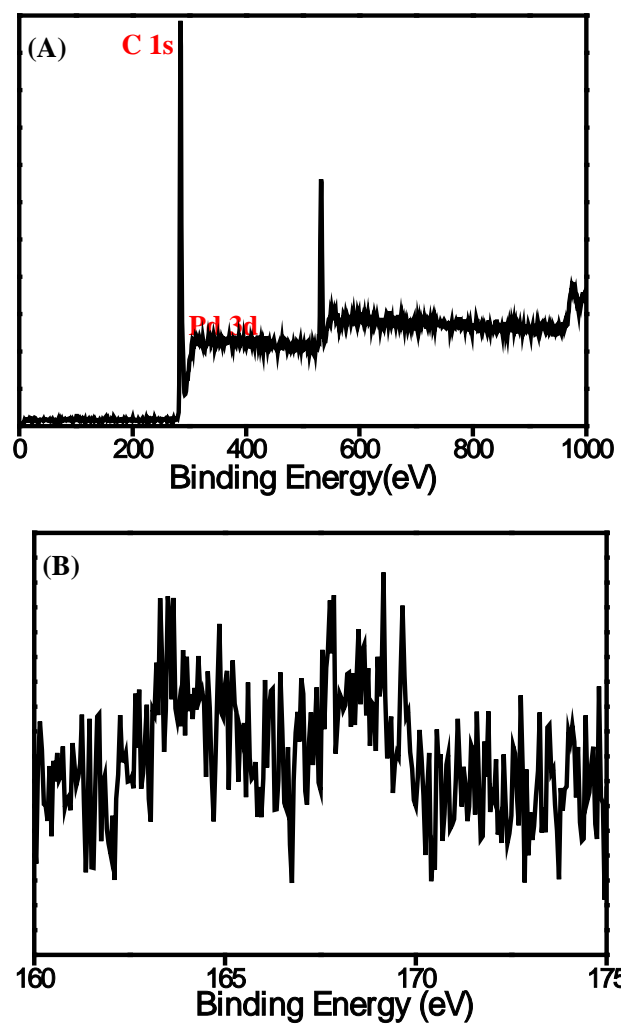
**Fig. S3** XRD patterns of the Pd<sub>6</sub>(C<sub>12</sub>H<sub>25</sub>S)<sub>12</sub> (black line), Pd<sub>6</sub>/AC (blue line), Pd<sub>6</sub>/AC-V (red line) and activated carbon (AC, green line).



**Fig. S4** (A) XPS survey spectrum of the  $\text{Pd}_6(\text{C}_{12}\text{H}_{25}\text{S})_{12}$  and (B) High resolution XPS of S 2p from the  $\text{Pd}_6(\text{C}_{12}\text{H}_{25}\text{S})_{12}$ .

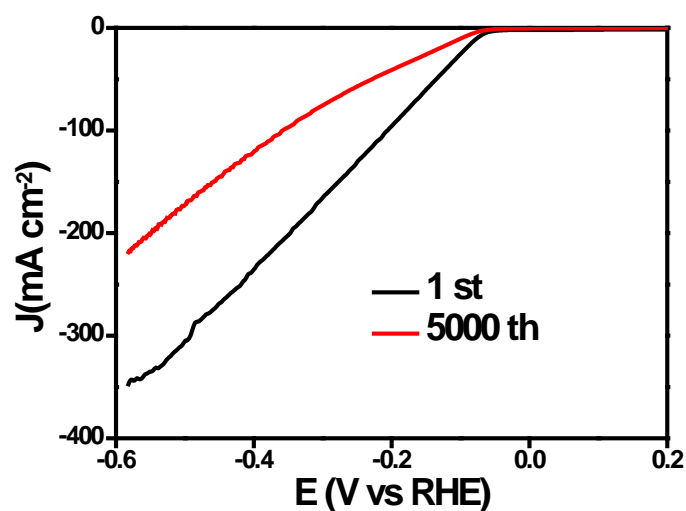


**Fig. S5** (A) XPS survey spectrum of the Pd<sub>6</sub>/AC and (B) High resolution XPS of S 2p from the Pd<sub>6</sub>/AC.

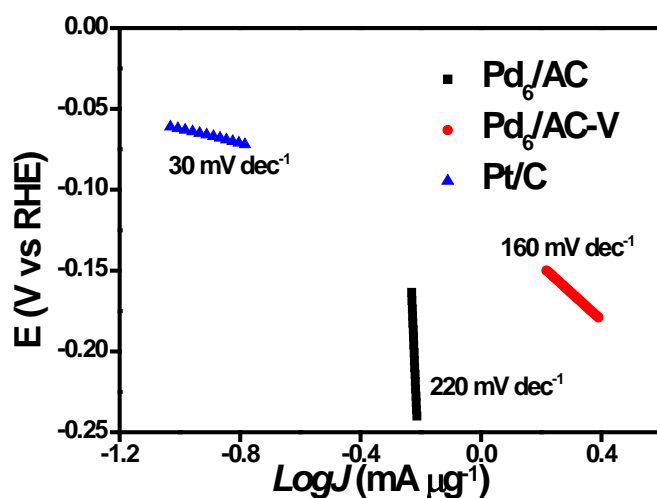


**Fig. S6** (A) XPS survey spectrum of the Pd<sub>6</sub>/AC-V and (B) High resolution XPS of S 2p from the Pd<sub>6</sub>/AC-V.



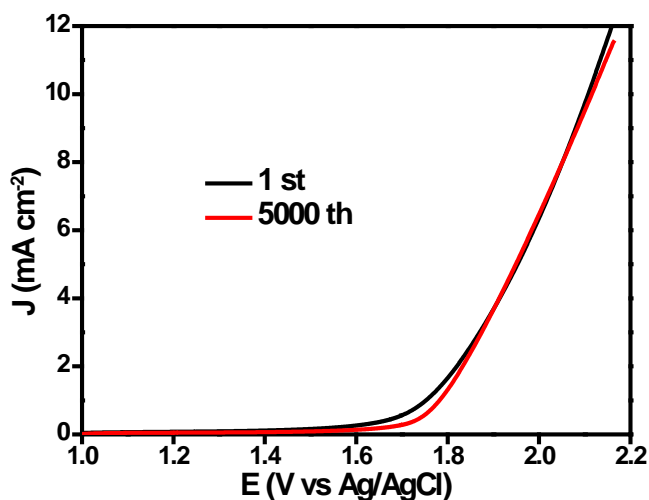


**Fig. S7** The polarization curves of the commercial Pt/C before and after 5000 potential cycles for HER.

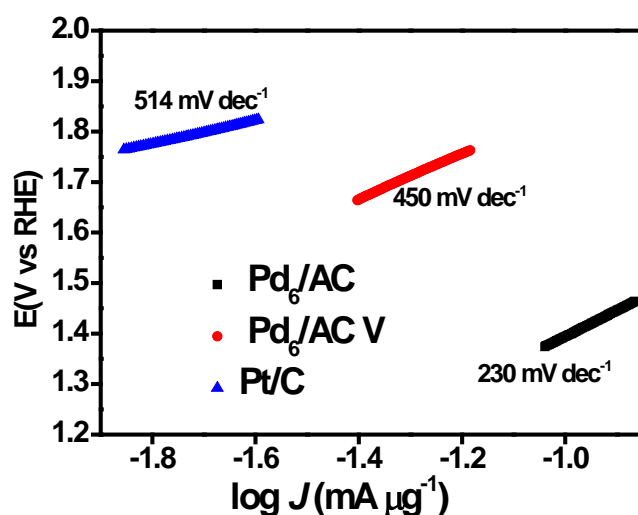


**Fig. S8** Tafel plots of the synthesized Pd<sub>6</sub>/AC, Pd<sub>6</sub>/AC-V and commercial Pt/C for HER.

Based on the Tafel slopes shown in Fig.S8, the studied catalysts show different control steps for HER. According to the previous report,<sup>2</sup> the discharge process is the determining step on the Pd<sub>6</sub>/AC and Pd<sub>6</sub>/AC-V catalysts. However, the reaction on the Pt/C is determined by Tafel recombination steps.



**Fig. S9** The polarization curves of the commercial Pt/C before and after 5000 potential cycles for OER.



**Fig. S10** Tafel curves of the synthesized Pd<sub>6</sub>/AC, Pd<sub>6</sub>/AC-V and commercial Pt/C for OER.

From Fig.S10, the Tafel slope increases in the order of the Pd<sub>6</sub>/AC, Pd<sub>6</sub>/AC-V and commercial Pt/C. Such result indicates the different catalytic reaction kinetics on the three catalysts, which may include the effects from the ligands. Meanwhile, the smaller Tafel slope of Pd<sub>6</sub>/AC is more favorable to the oxygen evolution reaction.

#### References:

1. Zhu, M.; Zhou, S. M.; Yao, C. H.; Liao, L. W.; Wu, Z. K., *Nanoscale* **2014**, *6*, 14195-14199.
2. W. F. Chen, J. T. Muckerman and E. Fujita, *Chem. Commun.*, **2013**, *49*, 8896-8909.