

Sulfurization-Induced Partially Amorphous Palladium Sulfide Nanosheets for Highly Efficient Electrochemical Hydrogen Evolution

Yihui Wang,^a Kai Xu,^a Zizeng Zhu,^a Wen Guo,^a Tingting Yu,^a Maoshuai He,^b
Wenxian Wei^{*c} and Tao Yang^{*a}

^a *School of Environmental and Chemical Engineering, Jiangsu Ocean University,
Lianyungang 222005, Jiangsu, China*

^b *State Key Laboratory of Eco-Chemical Engineering, Ministry of Education, College
of Chemistry and Molecular Engineering, Qingdao University of Science and
Technology, Qingdao 266042, Shandong, China*

^c *Testing Center, Yangzhou University, Yangzhou 225009, Jiangsu, China*

^{*}Corresponding author.

E-mail address: yangtao_hit@163.com, yangt@jou.edu.cn (T. Yang)

Experimental

Chemicals.

Palladium(II) acetylacetonate ($\text{Pd}(\text{acac})_2$), oleylamine(OAm), Sublimed sulfur were obtained from Aladdin Industrial Corporation. All the chemical reagents were directly used without any pre-treatments.

Synthesis of PdS nanosheets(NSs).

Two dimensional PdS nanosheets were synthesized through a two steps method. In a typical experiment, $\text{Pd}(\text{acac})_2$ (40mg, 0.131 mmol) was dissolved in 10 mL of OAm in a 25 mL three-necked, round bottom flask with stirring. The flask was degassed and carbon monoxide (CO) flow (120 mL min^{-1}) was then introduced below the solution surface. The flask was then immersed into an oil bath ($210 \text{ }^\circ\text{C}$). The solution became black quickly in the first several minutes, suggesting that Pd nanosheets were generated. A solution of OAm (2.0 mL) with sublimed sulfur (8 mg, 0.249 mmol) was then added into the above flask after 20 min of reaction. After another 60 min, the system was cooled to room temperature naturally. The product was obtained by centrifugation at 8,000 rpm for 5 min and washed with trichloromethane twice.

Characterization

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were analyzed using a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Morphology and defined structure of the products were determined by using transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM). Surface elements were analyzed by using X-ray photoelectron spectrometers (XPS, Thermo Scientific K-Alpha+). STEM-energy dispersive X-ray spectroscopy (STEM-EDS) elemental mapping and line-scanning profiling was performed to

examine the morphologies and chemical composition of the products.

Electrochemical measurements

All the electrochemical tests were performed with a three electrode cell on an Autolab potentiostat/galvanostat (PGSTAT-302N) workstation in 1 M KOH. A glassy carbon electrode (GC, $\phi = 5$ mm) was used as the working electrode, a graphite rod counter electrode and a Hg/HgO reference electrode were put in the separated compartment. Linear sweep voltammetry (LSV) measurements were carried out with scan rate of 5 mV s^{-1} and 1600 rpm rotating speed. All the measurements were measured at room temperature. The potentials presented here was calibrated relative to the reversible hydrogen electrode (RHE) using the below equations:

$$E (\text{V vs. RHE}) = E (\text{V vs. Hg/HgO}) + 0.0591 * \text{pH} + E^0_{\text{Hg/HgO}} (\text{V vs. SHE, } 25^\circ\text{C})$$

where, $E^0_{\text{Hg/HgO}}$ (V vs. SHE, 25°C) is 0.098 V.

The catalyst ink and the working electrode were prepared via the following procedure. A Nafion solution was prepared by dissolving Nafion (Sigma-Aldrich, 5 wt%, 25.0 μL) and isopropanol (1.0 mL) into deionized water (4.0 mL) via ultra-sonication (10 min). The catalyst inks were obtained by putting the carbon supported catalyst (5.0 mg) into the above Nafion solution (5.0 mL), respectively. 45 μL catalyst ink was deposited onto the GC electrode, and then dried naturally. Durability tests were performed by repeating LSV scans at a sweeping rate of 100 mV s^{-1} in 1.0 M KOH for 10000 cycles.

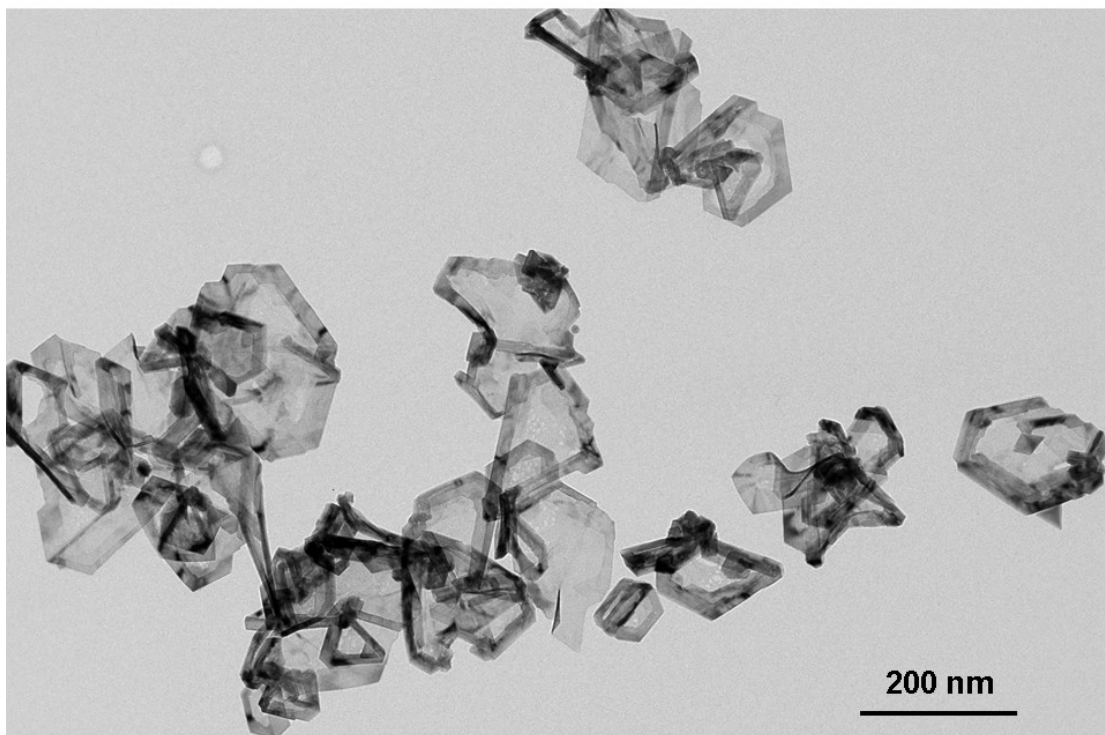


Fig. S1 TEM image of Pd nanosheets.

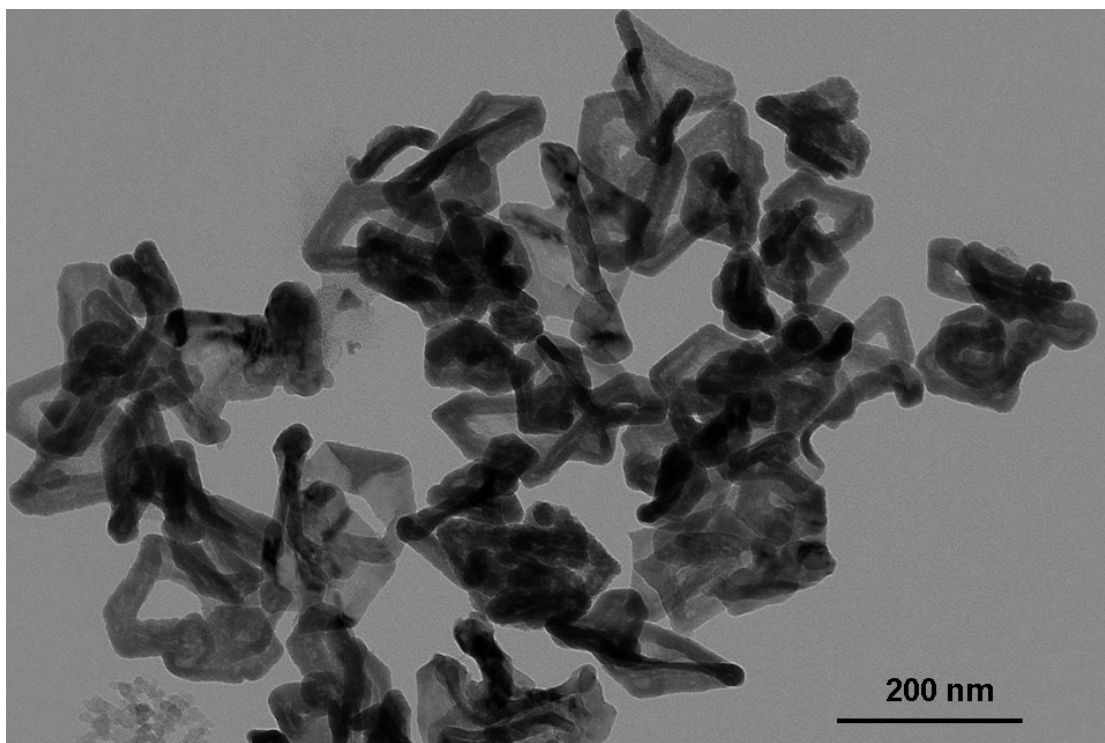


Fig. S2 TEM image of PdS nanosheets.

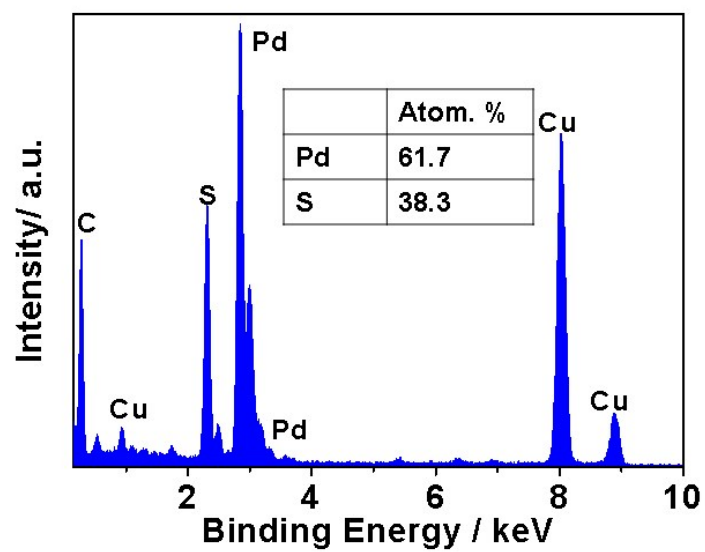


Fig. S3 EDS spectrum of PdS nanosheets

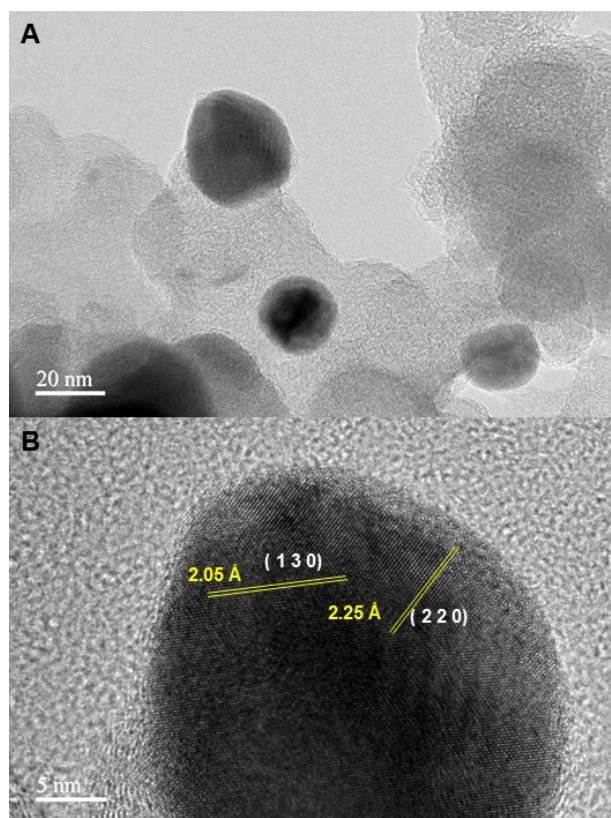


Figure S4. (A) TEM and (B) HRTEM images of PdS-550 NSs.

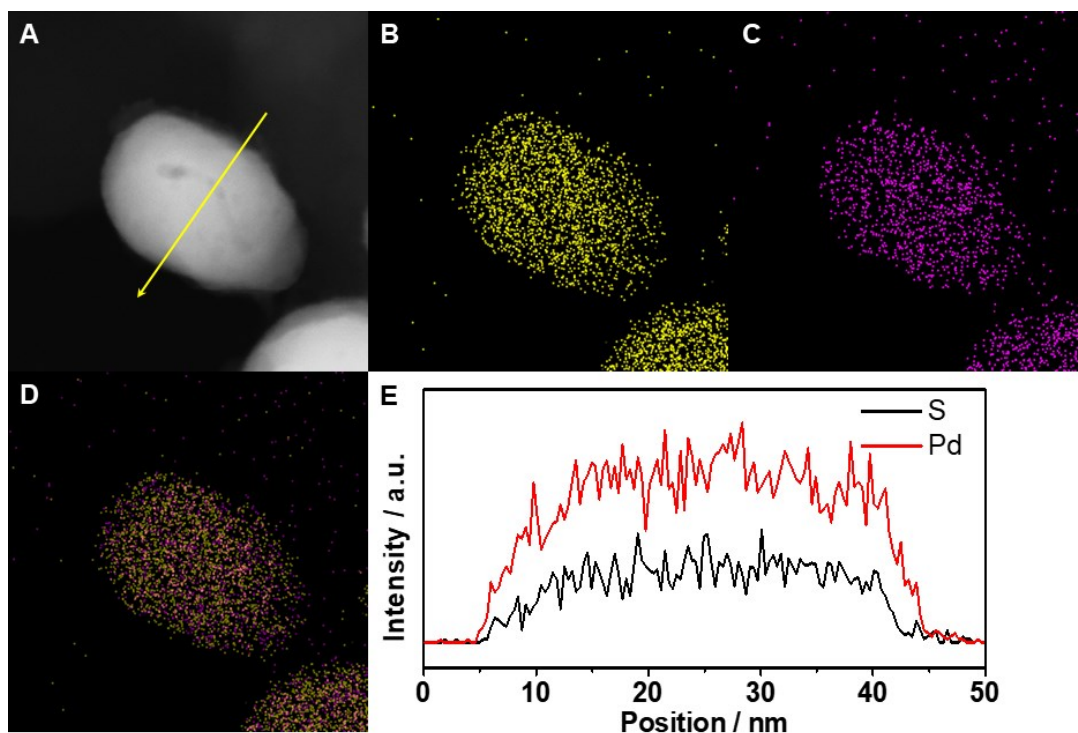


Figure S5. (A) STEM image of PdS-550 NSs and the corresponding elemental mapping of (B) Pd, (C) S and (D) the merged image, (E) EDX cross-sectional compositional line scanning.

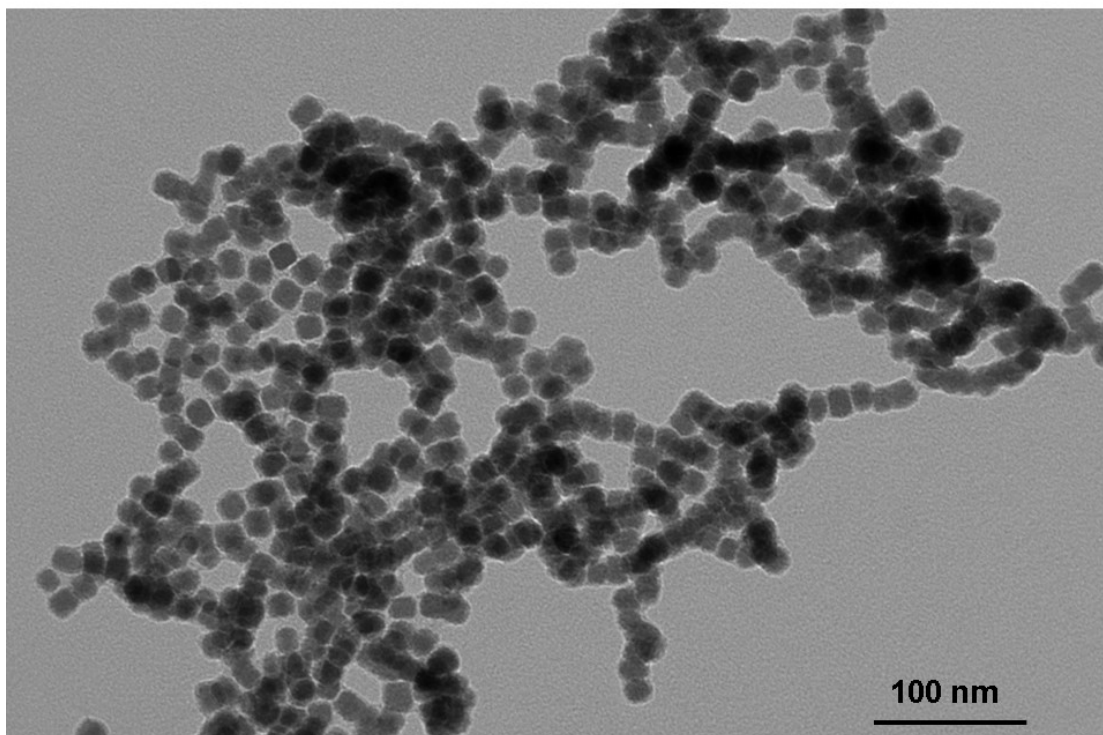


Fig. S6 TEM image of PdS nanoparticles. The PdS nanoparticles were synthesized through the following procedure. Pd nanocubes were firstly synthesized through a hydrothermal procedure. PVP (105 mg), ascorbic acid (65 mg) were dissolved in deionized water (8 mL) at 80 °C, Na_2PdCl_4 (57 mg) was dissolved in deionized water (3 mL) and then poured into the above solution. The reaction system was cooled to room temperature after 3 h. 1 mL of the above solution was re-dispersed in 9 mL DMF and 20 mg of thiourea (20 mg) was added. The mixture was held at 120 °C for 12 h. The final PdS nanoparticles were collected by centrifuge.

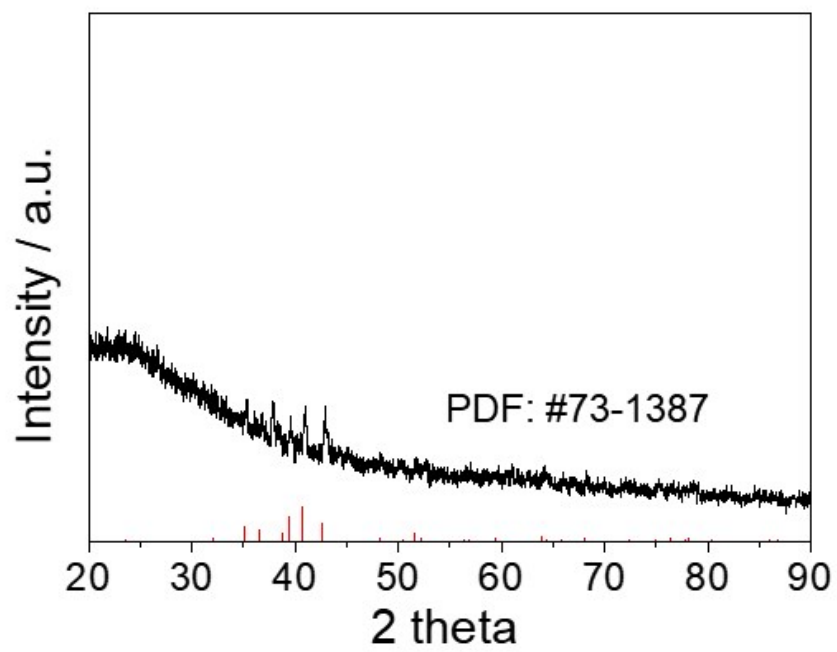


Fig. S7 XRD pattern of the PdS nanoparticles.

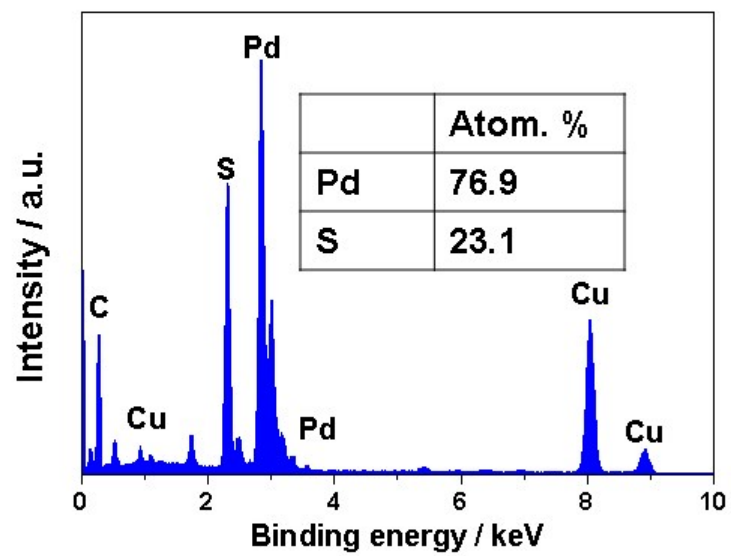


Fig. S8 EDS spectrum of PdS nanoparticles

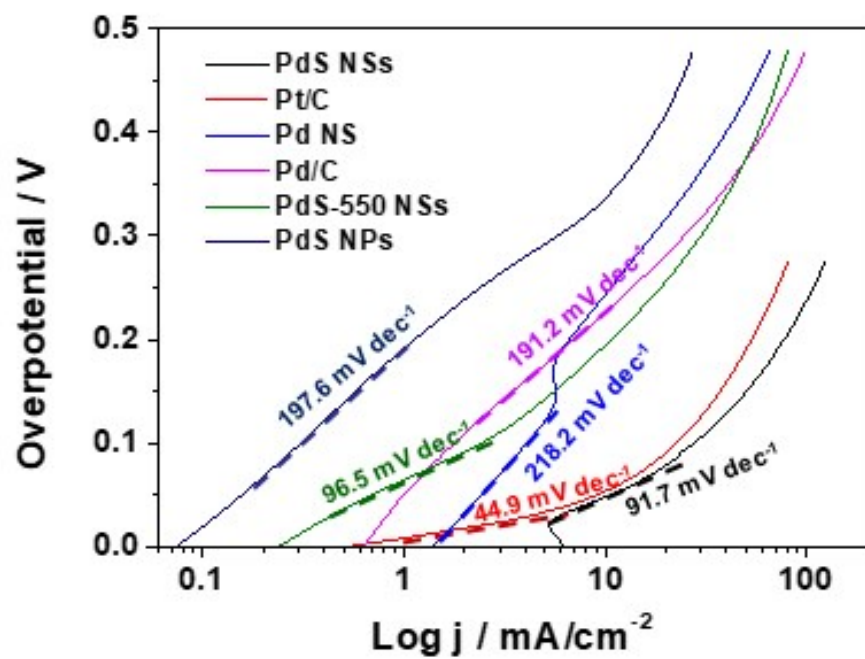


Fig. S9 Tafel curves of PdS NSs, PdS-550 NSs, PdS NPs, commercial Pd/C and Pt/C catalysts.

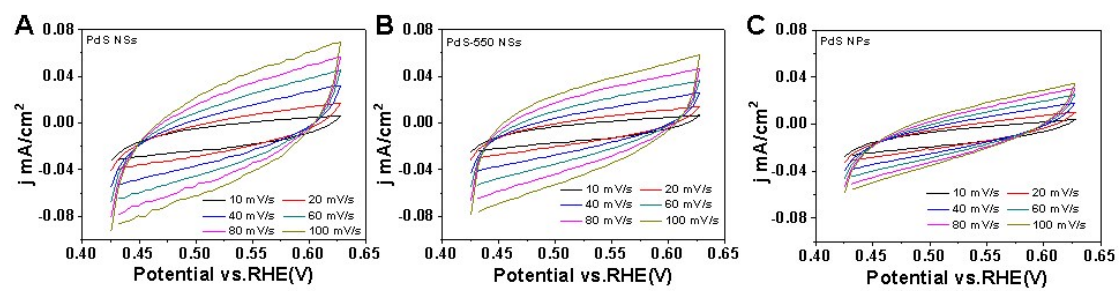


Fig. S10 CV curves of Pd NSs, PdS-550 NSs and PdS NPs at scanning rate of 10 mV/s, 20 mV/s, 40 mV/s, 60 mV/s, 80 mV/s and 100 mV/s.

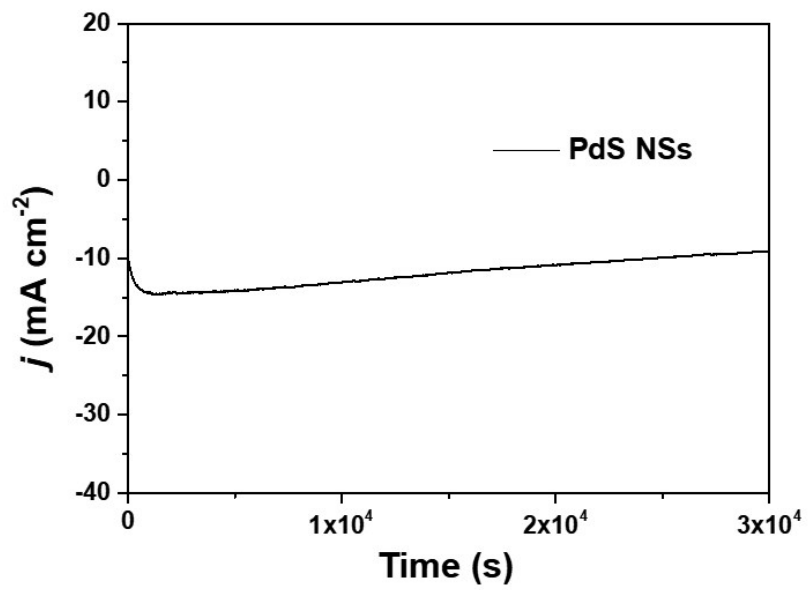


Figure S11. The i-t curve of PdS NSs.

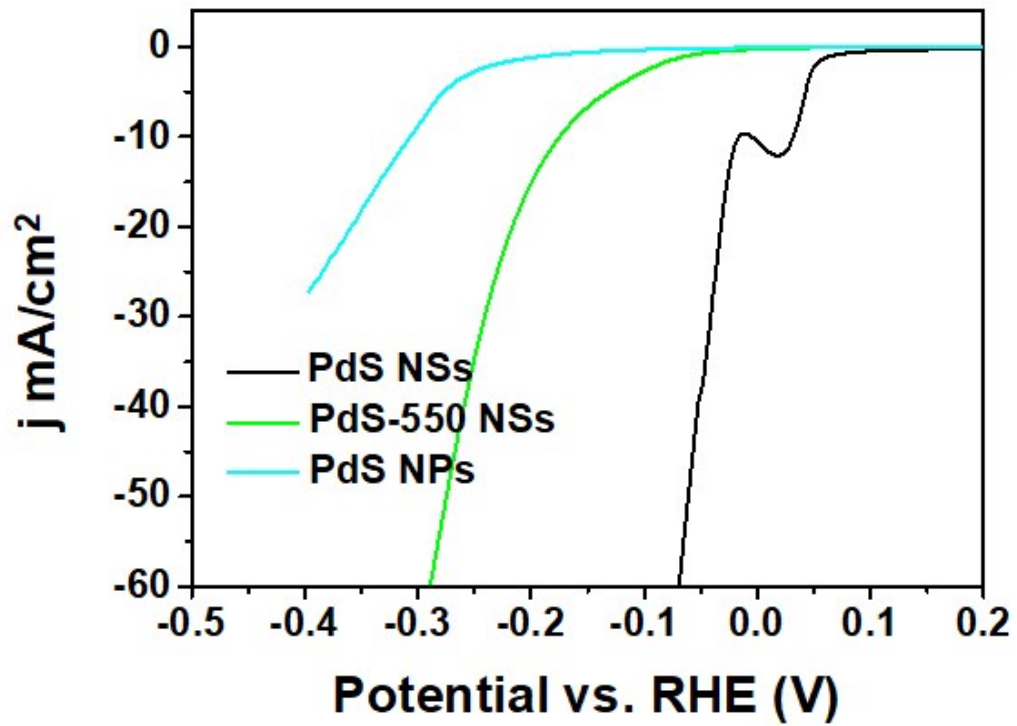


Fig. S12 HER polarization curves of PdS, PdS-550 NSs and PdS NPs with IR-compensation.

Table S1. The performances of different catalysts in the literatures.

Catalysts	Onset potential	$\eta@ 10\text{mA}$ cm^{-2}	Electrolyte	Tafel slope (mV dec^{-1})	Reference
PdS		49	1M KOH	91.7	This work
Pd _{3.02} Te @RGO	7	97	1M KOH	90	[1]
Pd@CN _x	12	55	0.5 M H ₂ SO ₄	35	[3]
PdCo@CN	-	80	0.5 M H ₂ SO ₄	31	[4]
PdNi nanoparticles	-	187	1 M KOH	93	[5]
PdCu nanocrystals	56	80	0.5 M H ₂ SO ₄	51	[6]
C/N-co-doped Pd@Ag	-	111	0.5 M H ₂ SO ₄	64	[7]
Pd ₁₇ Se ₁₅	80	182		57	
Pd ₇ Se ₄	70	162	0.5 M H ₂ SO ₄	56	[8]
Pd ₄ Se	30	94		50	
PdBi ₂	11	78	0.5M HClO ₄	63	[9]
Pd ₁₆ S ₇ /MoS ₂ /CNFs		83		113	
Pd ₁₆ S ₇ /CNFs	-	245	0.5 M H ₂ SO ₄	225	[10]
Pd/FeOx(OH) _{2-2x} NPs	~0	170	0.1 M KOH	150	[11]
Pd ₃ Ru/C	-	42	1 M KOH	-	[12]
Pd ₃ P _{0.95} NPs	-	75	1 M KOH	64	[13]
Pd doped Ni alloys	-	50	1 M KOH	102	[14]

References

- [1] Jiao L, Li F, Li X, Ren R, Li J, Zhou X, et al. Ultrathin pdte nanowires anchoring reduced graphene oxide cathodes for efficient hydrogen evolution reaction[J]. *Nanoscale*, 2015. 7(44): 18441-18445.
- [2] Yang H, Tang Z, Wang K, Wu W, Chen Y, Ding Z, et al. Co@pd core-shell nanoparticles embedded in nitrogen-doped porous carbon as dual functional electrocatalysts for both oxygen reduction and hydrogen evolution reactions[J]. *Journal of Colloid and Interface Science*, 2018. 528: 18-26.
- [3] Bhowmik T, Kundu M K, Barman S. Palladium nanoparticle–graphitic carbon nitride porous synergistic catalyst for hydrogen evolution/oxidation reactions over a broad range of ph and correlation of its catalytic activity with measured hydrogen binding energy[J]. *ACS Catalysis*, 2016. 6(3): 1929-1941.
- [4] Chen J, Xia G, Jiang P, Yang Y, Li R, Shi R, et al. Active and durable hydrogen evolution reaction catalyst derived from pd-doped metal–organic frameworks[J]. *ACS Applied Materials & Interfaces*, 2016. 8(21): 13378-13383.
- [5] Chen J, Chen J, Yu D, Zhang M, Zhu H, Du M. Carbon nanofiber-supported pdni alloy nanoparticles as highly efficient bifunctional catalysts for hydrogen and oxygen evolution reactions[J]. *Electrochimica Acta*, 2017. 246: 17-26.
- [6] Wang R, Jiang L-Y, Feng J-J, Liu W-D, Yuan J, Wang A-J. One-pot solvothermal synthesis of pdcu nanocrystals with enhanced electrocatalytic activity toward glycerol oxidation and hydrogen evolution[J]. *International Journal of Hydrogen Energy*, 2017. 42(10): 6695-6704.
- [7] Liu Y-Y, Zhang H-P, Zhu B, Zhang H-W, Fan L-D, Chai X-Y, et al. C/n-co-doped pd

coated ag nanowires as a high-performance electrocatalyst for hydrogen evolution reaction[J].

Electrochimica Acta, 2018. 283: 221-227.

[8] Kukunuri S, Austeria P M, Sampath S. Electrically conducting palladium selenide (pd₄se, pd₁₇se₁₅, pd₇se₄) phases: Synthesis and activity towards hydrogen evolution reaction[J]. *Chemical Communications*, 2016. 52(1): 206-209.

[9] Sarkar S, Subbarao U, Peter S C. Evolution of dealloyed pdbi₂ nanoparticles as electrocatalysts with enhanced activity and remarkable durability in hydrogen evolution reactions[J]. *Journal of Materials Chemistry A*, 2017. 5(30): 15950-15960.

[10] Wen Y, Zhu H, Zhang L, Hao J, Wang C, Zhang S, et al. Beyond colloidal synthesis: Nanofiber reactor to design self-supported core-shell pd₁₆s₇/mos₂/cnfs electrode for efficient and durable hydrogen evolution catalysis[J]. *ACS Applied Energy Materials*, 2019. 2(3): 2013-2021.

[11] Liao H, Wei C, Wang J, Fisher A, Sritharan T, Feng Z, et al. A multisite strategy for enhancing the hydrogen evolution reaction on a nano-pd surface in alkaline media[J]. *Advanced Energy Materials*, 2017. 7(21).

[12] Qin X, Zhang L, Xu G-L, Zhu S, Wang Q, Gu M, et al. The role of ru in improving the activity of pd toward hydrogen evolution and oxidation reactions in alkaline solutions[J]. *ACS Catalysis*, 2019. 9(10): 9614-9621.

[13] Xia T, Zhao M, Tong B, Kang Z, Wu Y, Ding W, et al. Synthesis of pdp nanoparticles as electrocatalysts for hydrogen evolution reaction in an alkaline medium[J]. *Nano*, 2019. 14(05).

[14] Nie M, Xue Z H, Sun H, Liao J M, Xue F J, Wang X X. Pd doped ni derived from ni - metal organic framework for efficient hydrogen evolution reaction in alkaline electrolyte[J]. *International Journal of Hydrogen Energy*, 2020. 45(53): 28870-28875.