# Supporting information for

# *Atomic layer deposition of Pd nanoparticles and single atoms on self-supported carbon monolithic catalysts synergistically boost hydrogen evolution reaction*

Bin Zhang, Xulong Song, Zhiheng Wang, Binbin Xu, Tuo Ji, Lilong Zhang, Xiaohua Lu, and Jiahua Zhu*

State key Laboratory of Materials-oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China

*Corresponding author. J.Z. E-mail: jhzhu@njtech.edu.cn

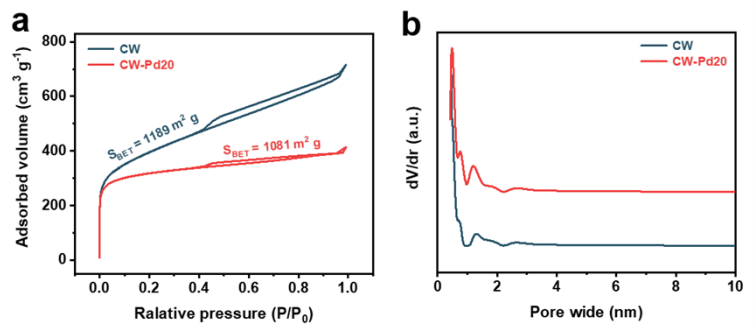


**Figure S1.** (a) $N_2$ adsorption/desorption isotherms and (b) pore size distribution of CW and CW-Pd20.

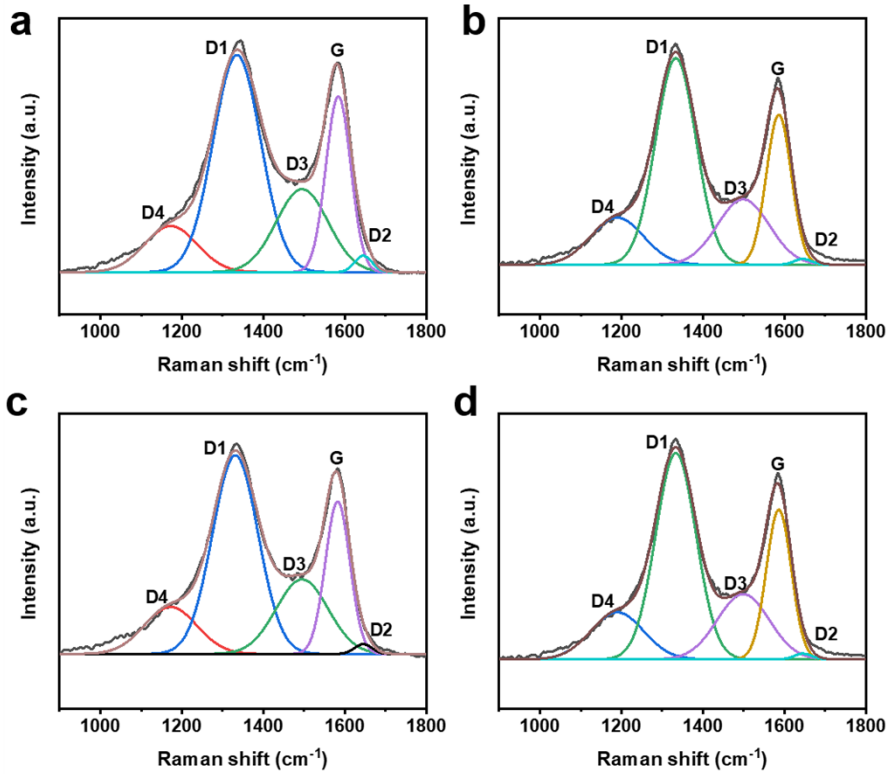


**Figure S2.** Raman spectra deconvolution results of a) CW, b) CW-Pd10, c) CW-Pd20, d) CW-Pd30.

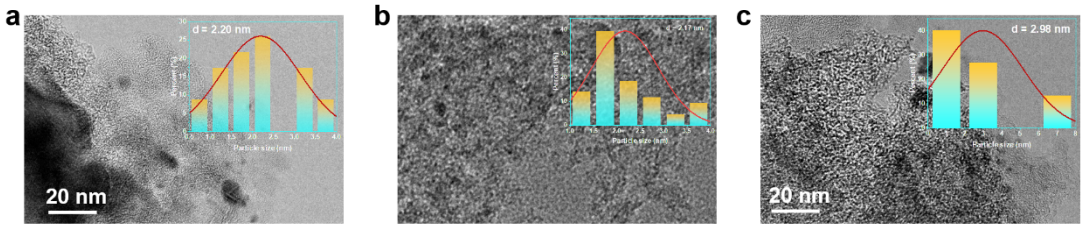


**Figure S3.** TEM images and size distribution (inset) of a) CW-Pd10, b) CW-Pd20, c) CW-Pd30.

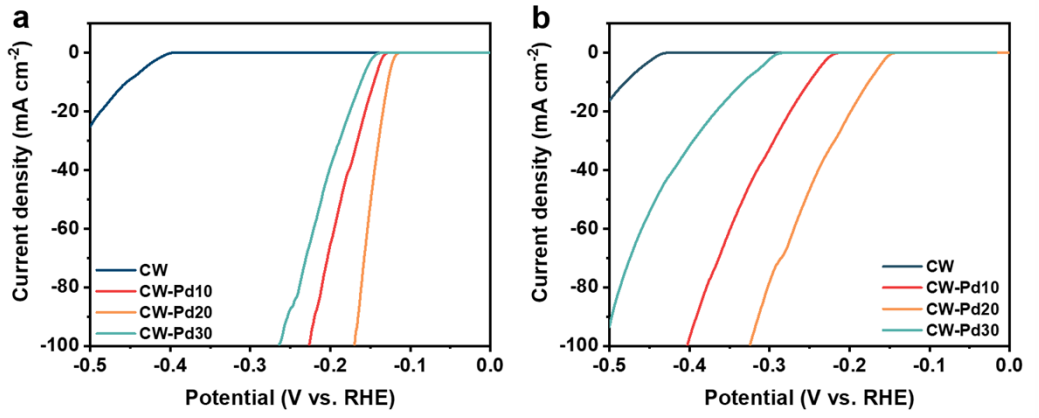


**Figure S4.** LSV curves of CW and CW-Pd with different ALD cycles in a) 0.5M $H_2SO_4$, b) 1M PBS (PH = 7.2)

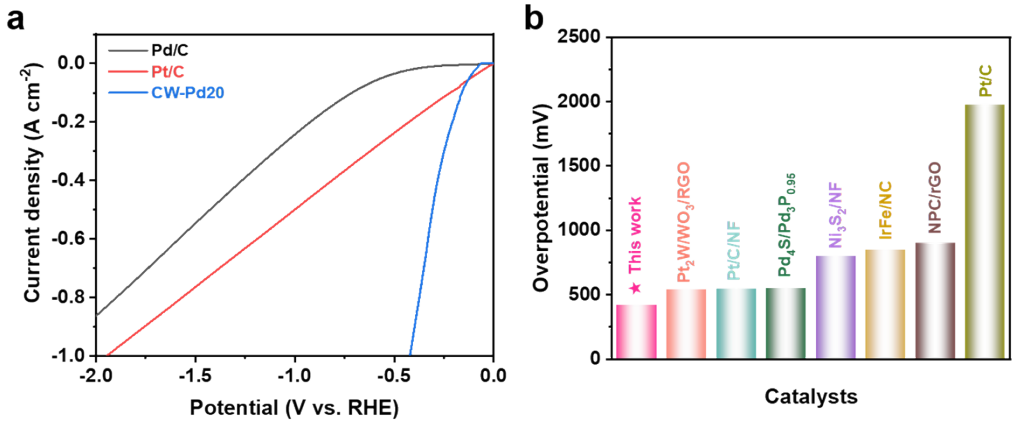


**Figure S5.** (a) LSV curves of CW-Pd20, commercial Pt/C and Pd/C in 1M KOH. (b) the comparison of overpotentials at 1 A $cm^{-2}$ for CW-Pd20 and other reported electrocatalysts[1-6].

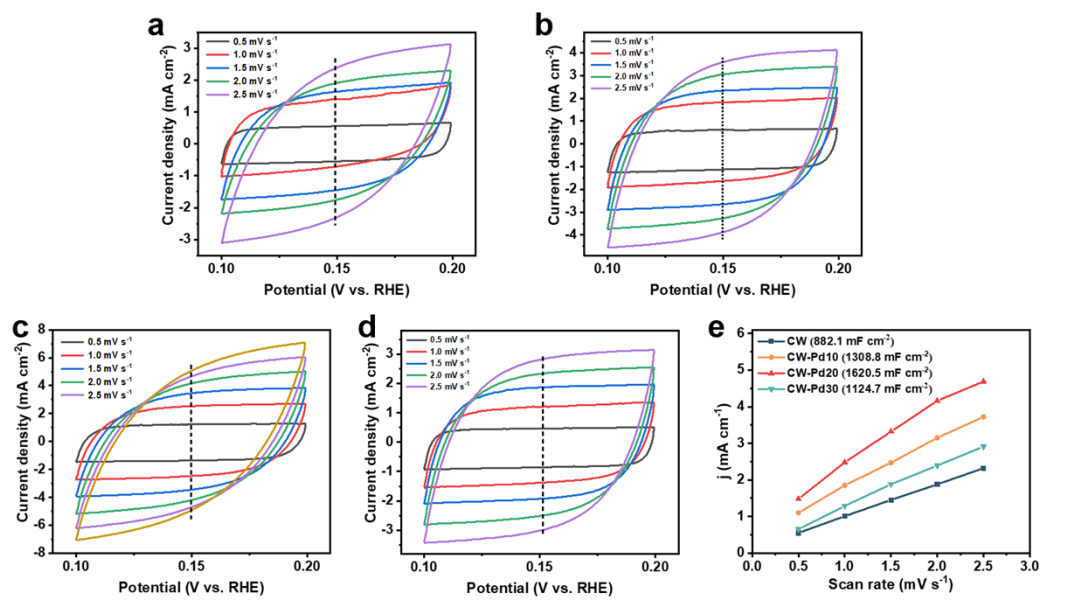


**Figure S6.** CV curves of a) CW, b) CW-Pd10, c) CW-Pd20, d) CW-Pd30. e) The electrochemical double-layer capacitance for CW and CW-Pd with different ALD cycles.

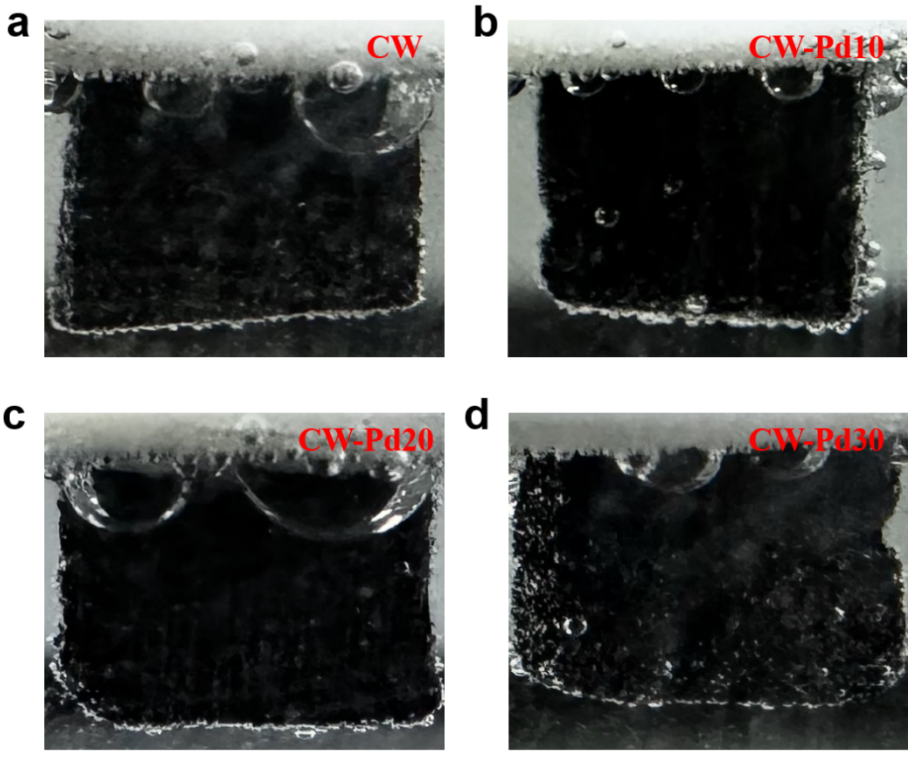


**Figure S7.** The optical figures of a) CW, b) CW-Pd10, c) CW-Pd20, d) CW-Pd30 during HER process.

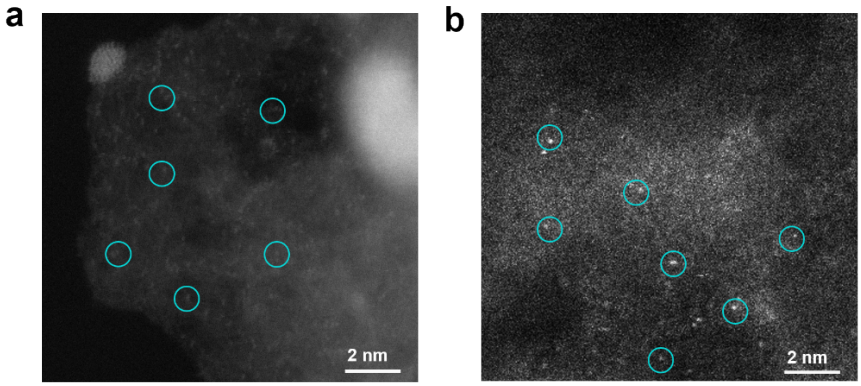


**Figure S8**. The HAADF-STEM images of CW-Pd20 (a) before and (b) after 40h stability test.

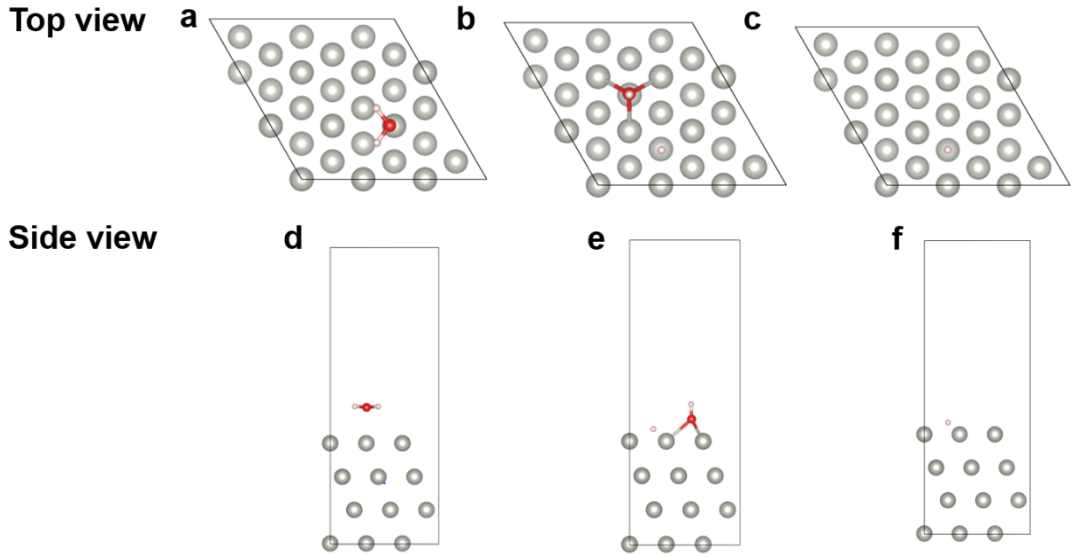


**Figure S9.** Optimized structure of a, d) $H_2O$ adsorbed, b, e) $H_2O$ dissociate, c, f) H adsorbed on Pd (111) containing 4 slabs with 12 Å vacuum layer.

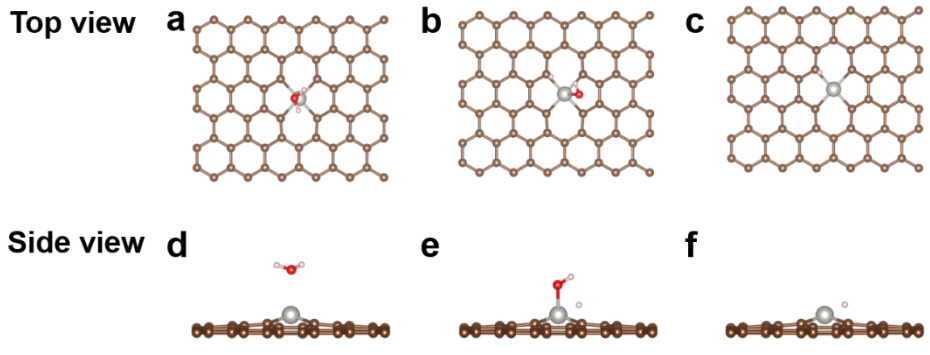


**Figure S10.** Optimized structure of a, d) $H_2O$ adsorbed, b, e) $H_2O$ dissociate, c, f) H adsorbed on $Pd_{SA}$ with 12 Å vacuum layer.

**Table S1.** The Raman fitting results of CW and CW-Pd.

| | D1 | D2 | D3 | D4 | G | D1+D4 |
|---|---|---|---|---|---|---|
| CW | 46.9 | 0.9 | 20.0 | 12.8 | 19.4 | 59.7 |
| CW-Pd10 | 48.0 | 1.7 | 19.7 | 11.4 | 19.2 | 59.4 |
| CW-Pd20 | 46.9 | 0.9 | 20.0 | 12.8 | 19.4 | 59.7 |
| CW-Pd30 | 46.2 | 0.6 | 18.8 | 13.7 | 20.7 | 59.9 |

**Table S2.** Elemental composition of the CW-Pd20 from XPS.

| **Catalyst** | **Pd (wt. %)** | **C (wt. %)** | **O (wt. %)** |
|---|---|---|---|
| CW-Pd20 | 0.2 | 93.9 | 5.9 |

**Table S3.** Structure information of CW-Pd20 extracted from EXAFS fitting.

| path | N | R | $E_0$ | sigma^2 | R-factor |
|---|---|---|---|---|---|
| Pd-C/O | 0.73±0.61 | 2.16±0.082 | 19.7±7.1 | 0.001 | 0.015 |
| Pd-Pd | 4.61±0.9 | 2.73±0.006 | 4.61±0.9 | 0.005 | |

**Reference**


1. Y. W. Peng, C. Shan, H. J. Wang, L. Y. Hong, S. Yao, R. J. Wu, Z. M. Zhang and T. B. Lu, *Advanced Energy Materials*, 2019, **9,** 1900597.
2. G. Zhang, A. Wang, L. Niu, W. Gao, W. Hu, Z. Liu, R. Wang and J. Chen, *Advanced Energy Materials*, 2022, **12** 2103511.
3. K. Sun, L. Zeng, S. Liu, L. Zhao, H. Zhu, J. Zhao, Z. Liu, D. Cao, Y. Hou, Y. Liu, Y. Pan and C. Liu, *Nano Energy*, 2019, **58**, 862-869.
4. G. Li, J. Yu, J. Jia, L. Yang, L. Zhao, W. Zhou and H. Liu, *Advanced Functional Materials*, 2018, **28**, 1801332.
5. W. He, R. Zhang, D. Cao, Y. Li, J. Zhang, Q. Hao, H. Liu, J. Zhao and H. L. Xin, *Small*, 2022, **19**, 2205719.

6. P. Jiang, H. Huang, J. Diao, S. Gong, S. Chen, J. Lu, C. Wang, Z. Sun, G. Xia, K. Yang, Y. Yang, L. Wei and Q. Chen, *Applied Catalysis B: Environmental*, 2019, **258**, 117965.