

## Electronic Supplementary Information for

### Identifying the Rate-determining Step of the Electrocatalytic Hydrodechlorination Reaction on Palladium Nanoparticles

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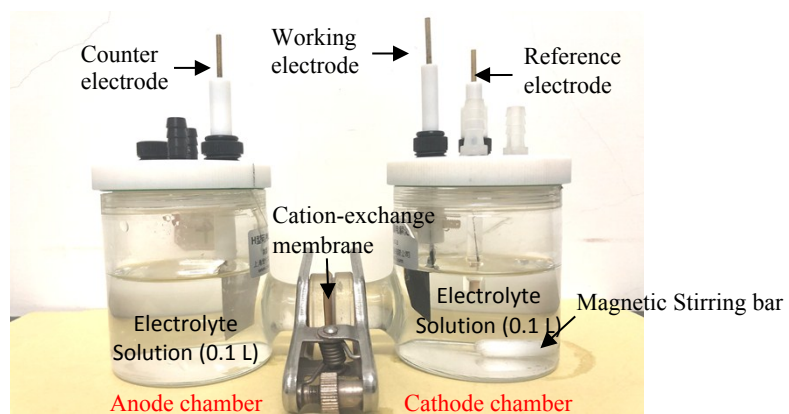
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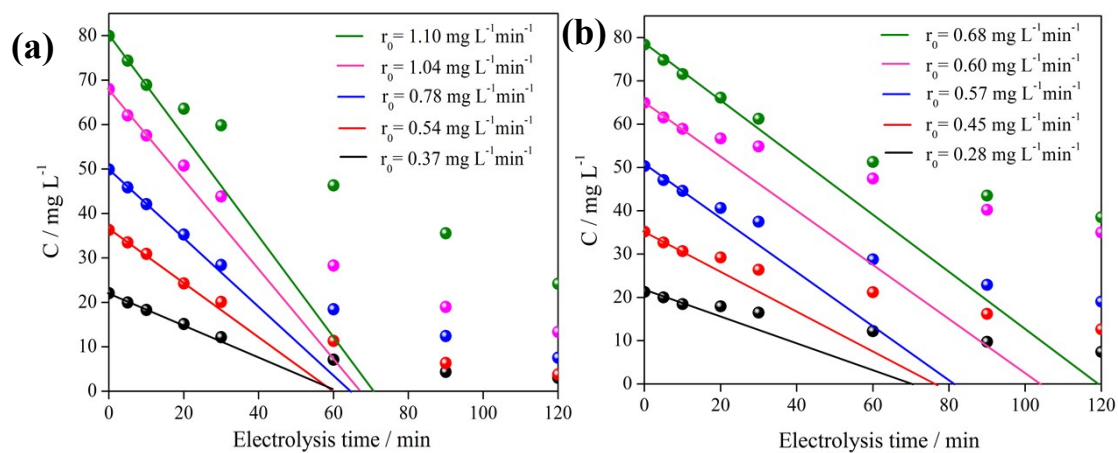
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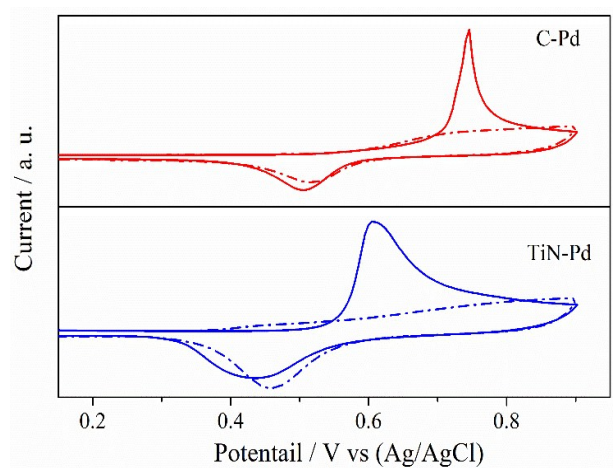
This supplementary material is an 11-page document, which consists of 8 Figures and 1 Table.



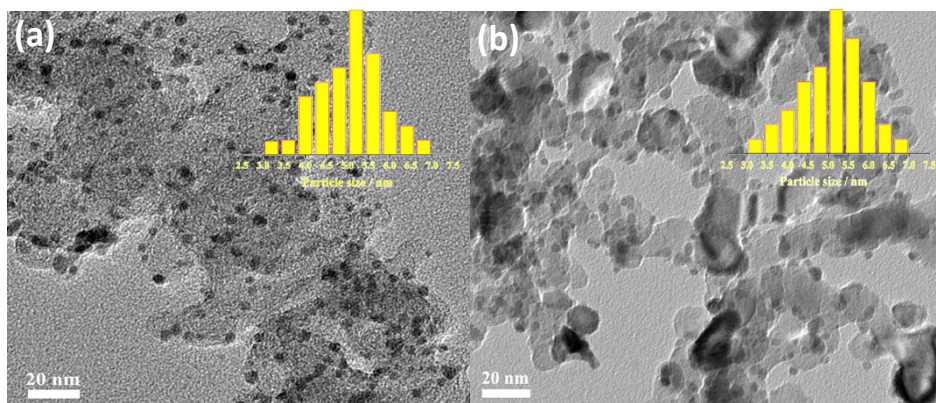
**Fig S1.** The photo of our H-shaped electrochemical cell with the electrodes, electrolyte solution and cation-exchange membrane.



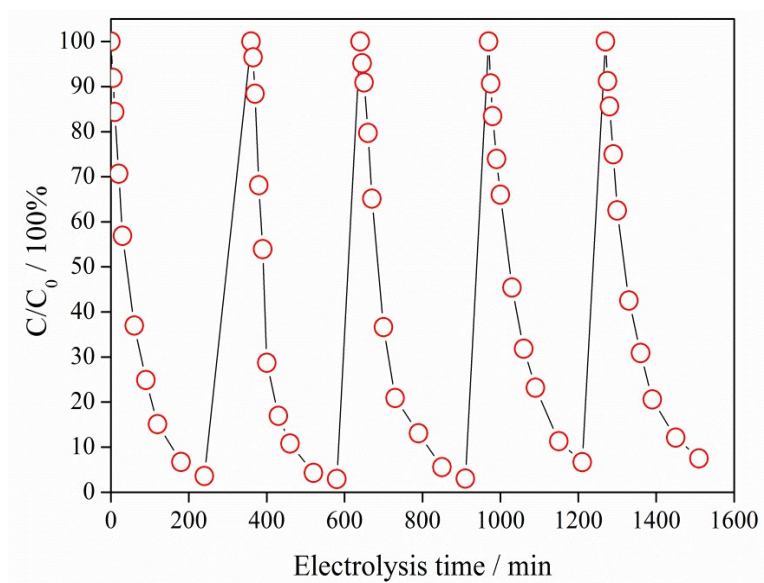
**Fig S2.** Variation in the concentration of 2,4-DCP with electrolysis time in the initial 120 min of EHDC reactions on (a) TiN-Pd and (b) C-Pd.



**Fig S3.** CO stripping voltammograms on TiN-Pd and C-Pd catalysts in 0.1 M HClO<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup>.



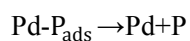
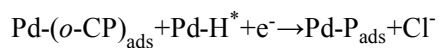
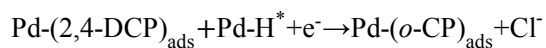
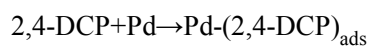
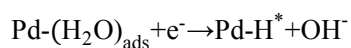
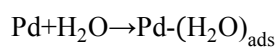
**Fig S4.** Representative TEM images of the (a) C-Pd and (b) TiN-Pd after the EHDC test.



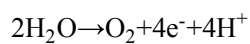
**Fig S5.** Durability test for TiN-Pd by repeating the EHDC reactions under a cathode potential of -0.80 V in a N<sub>2</sub>-saturated 50 mM Na<sub>2</sub>SO<sub>4</sub> solution containing 50 mg L<sup>-1</sup> of 2,4-DCP.

## Electrochemical reaction on cathode and anode

EHDC took place on cathode<sup>[1]</sup>:



OER (oxygen evolution reaction) occurred on anode<sup>[2]</sup>:



## References:

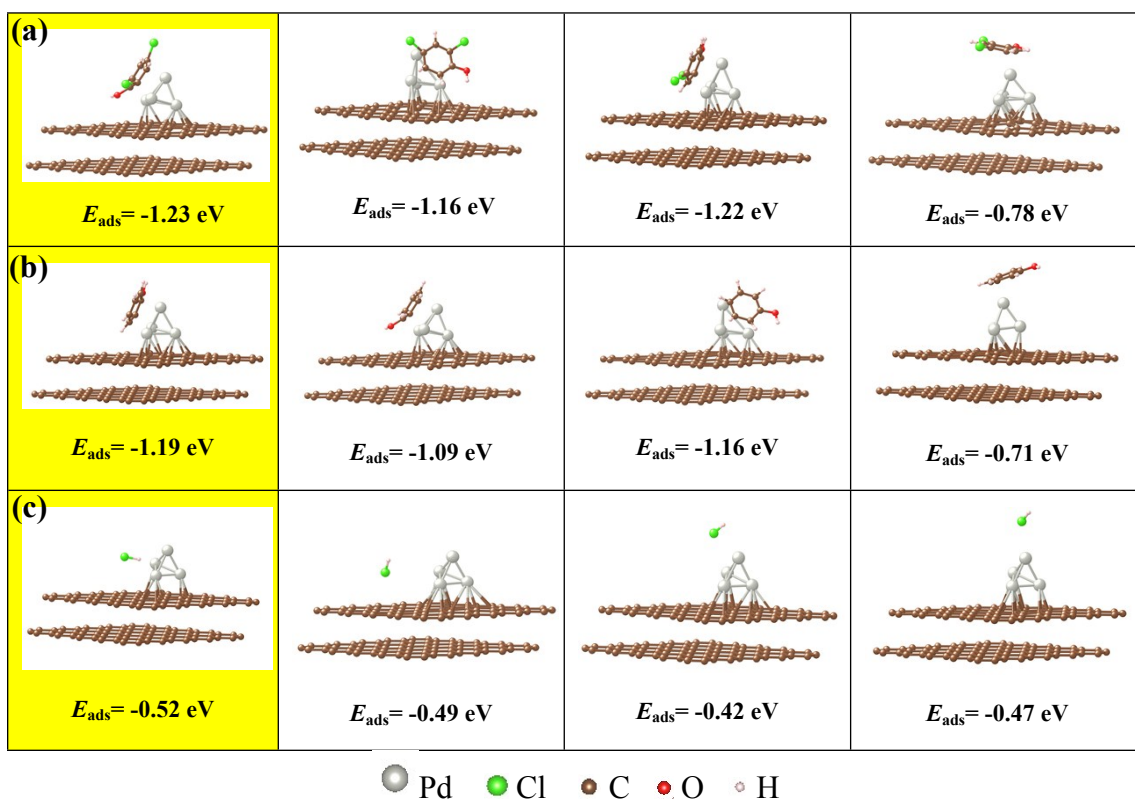
[1] Li, A.; Zhao, X.; Hou, Y.; Liu, H.; Wu, L.; Qu, J., The electrocatalytic dechlorination of chloroacetic acids at electrodeposited Pd/Fe-modified carbon paper electrode. *Appl. Catal. B: Environ.* **2012**, *111*, 628-635.

[2] Reier, T.; Oezaslan, M.; & Strasser, P., Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: a comparative study of nanoparticles and bulk materials. *Acs Catal.* **2012**, *2(8)*, 1765-1772.

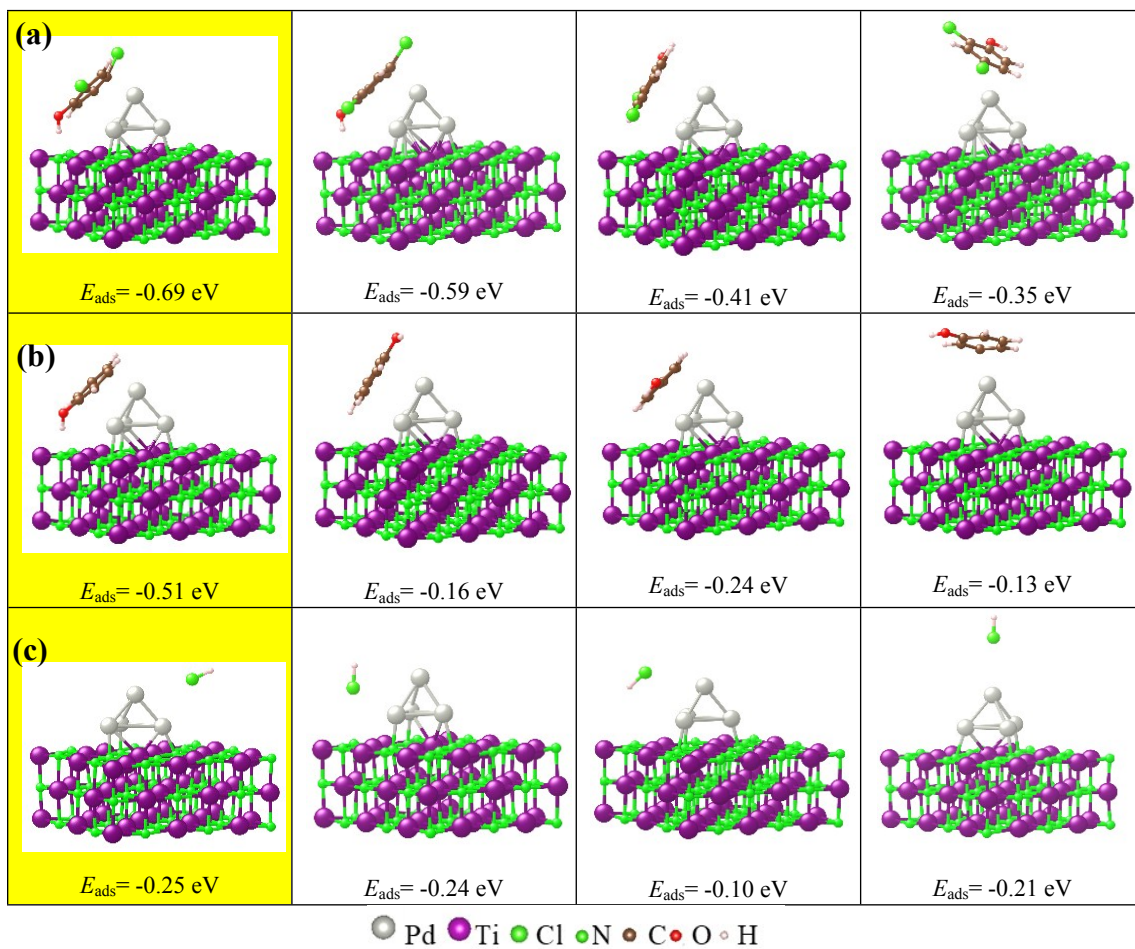
**Table S1.** The key parameters for TiN-Pd and C-Pd in L-H model

	C-Pd	TiN-Pd
$K / \text{L mg}^{-1}$	0.01067	0.00373
$k_r / \text{mg L}^{-1} \text{min}^{-1}$	1.54775	4.86192

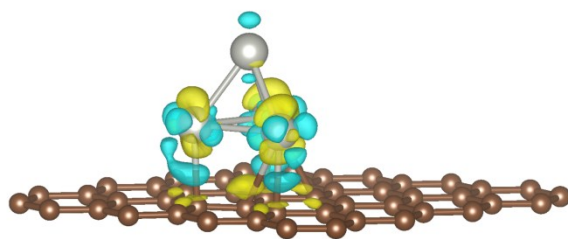




**Fig S6.** The adsorption energies of (a) 2,4-DCP, (b) P and (c) HCl on C-Pd in different adsorption configurations.



**Fig S7.** (a) The adsorption energy of 2,4-DCP on TiN-Pd in different adsorption configurations; (b) The adsorption energy of P on TiN-Pd in different adsorption configurations.



**Fig. S8.** The three-dimensional isosurfaces of charge density difference at the interface of Pd<sub>4</sub> and carbon layer.