**Supporting Information** 

## Facile Synthesis of Palladium Hierarchical Nanosheet Assemblies: Unraveling the Aggregation-Induced Synergistic Effect for Enhanced Methanol Oxidation Reaction Activity

Lijuan Han, Yuanyuan Min, Yingying Wang,\* Feng Liu, Maochang Liu, and Yiqun Zheng\*

<sup>a</sup> School of Chemistry, Chemical Engineering, and Materials, Jining University, Qufu, Shandong
 273155, China

<sup>b</sup> Health Management Department, Shandong Vocational College of Light Industry, Zibo, Shandong 255300, China.

<sup>c</sup> International Research Center for Renewable Energy, National Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

\*Corresponding authors: Prof. Dr. Y. Zheng, E-mail: <u>yzheng@jnxy.edu.cn</u>; Prof. Dr. Y.-Y. Wang, <u>hxwyy2005@mail.sdu.edu.cn</u>.



Figure S1. TEM image of Pd nanostructures synthesized using the same protocol as Pd HNAs but with an increased volume of aqueous  $Na_2PdCl_4$  precursor solution (20 mM, 250  $\mu$ L).



**Figure S2.** a-e) Histograms showing the size distribution of Pd HNAs with different volumes of aqueous Na<sub>2</sub>PdCl<sub>4</sub> (20 mM) solution: (a) 10 µL, (b) 20 µL, (c) 50 µL, (d) 125 µL, (e) 250 µL. f) Corresponding fitting plot. The fitting equation is as follows:  $y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}}$ , where the fitted parameters are: a= 169±43.9, b=0.97±0.64, and c=0.084±0.28.



Figure S3. TEM image of Pd nanocubes.



**Figure S4.** CV curves in 1 M methanol+1 M KOH with different scan rates: (a) Pd HNAs/C; (b) Pd nanocubes/C; (c) Pt/C. (d) Diagram showing the MOR kinetics based on specific activities and square root of scan rates.



Figure S5. TEM image of Pd HNAs after CA measurement.

Table S1. Summary of the relative peak areas (%) for each split B.E. peak and the parameters used

Orbital	Spectral line	B. E. Peak (eV)	FWHM (eV)	relative peak area	element/ oxidation state
Pd 3d	3d <sub>5/2</sub>	335.34	1.26	43.1%	Pd (0)
	3d <sub>5/2</sub>	337.49	1.57	14.2%	Pd (II)
	3d <sub>3/2</sub>	340.53	1.11	24.5%	Pd (0)
	3d <sub>3/2</sub>	342.32	2.22	18.2%	Pd (II)

to fit the Pd 3d high-resolution XPS spectra.

	Es	E <sub>p</sub>	ECSA	$j_r/j_f$	Specific Activity	Mass Activity	<i>j</i> (t=3000s)
Electrocatalyst	(mV)	(mV)	$(\mathrm{cm}^2 \mathrm{mg}^{-1})$		(mA cm <sup>-2</sup> )	(mA mg <sup>-1</sup> )	(mA mg <sup>-1</sup> )
Pd HNAs/C	450	0.808	143.9	0.572	1.92	276.1	4.62
Pd nanocubes/C	458	0.807	85.8	0.556	1.16	98.92	9.10
Pt/C	350	0.426	272.3	0.446	0.48	129.76	55.03

 Table S2. Summary of MOR performances of Pd HNAs/C, Pd nanocubes/C, Pt/C electrocatalysts in

 the present study.