## **Supporting Information**

for

Ultrafine Pd Particles Embedded in Nitrogen-enriched Mesoporous Carbon for Efficient

H<sub>2</sub> Production from Formic Acid Decomposition

Jingya Sun, Hao Qiu, Wugang Cao, Heyun Fu, Haiqin Wan\*, Zhaoyi Xu, Shourong

Zheng

State Key Laboratory of Pollution Control and Resource Reuse, Jiangsu Key Laboratory

of Vehicle Emissions Control, School of the Environment, Nanjing University, No. 22

Hankou Rd., Gulou District, Nanjing, Jiangsu, 210093, China

\*Corresponding author. Tel: +86-25-89680369; Fax: +86-25-89680596.

*E-mail*: wanhq@nju.edu.cn

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Sample	$\frac{S_{BET}}{m^2/g}$	Volume cm <sup>3</sup> /g	Average pore diameter nm
NMC-400	36.0	0.03	3.4
NMC-500	292.8	0.28	3.8
NMC-600	384.3	0.42	4.3
NMC-700	435.9	0.47	4.4
NMC-800	412.8	0.49	4.7
MC-600	987.6	1.04	4.2
SBA-15	532.1	0.88	6.4

Table S1. Surface areas, pore volumes and mesopore diameters of supports

Sample	$S_{BET}$ $m^2/g$	Volume cm <sup>3</sup> /g	Average pore diameter nm
Pd/NMC-400	22.6	0.02	3.8
Pd/NMC-500	269.6	0.30	4.0
Pd/NMC-600	321.6	0.34	4.3
Pd/NMC-700	431.6	0.48	4.4
Pd/NMC-800	397.4	0.47	4.9
Pd/MC-600	923.5	0.96	4.2

Table S2. Surface areas, pore volumes and mesopore diameters of supported Pd catalysts

Catalysts	Pyridinic N (%) 398.5 eV	Amine N (%) 399.2 eV	Pyrrole N (%) 400.2 eV	Graphitic N (%) 401.0 eV	Pyridinic oxide (%) 403.0 eV
Pd/NMC-400	47.3	11.3	27.2	14.2	0
Pd/NMC-500	44.1	10.3	25.6	19.9	0
Pd/NMC-600	44.0	7.5	20.9	24.1	3.5
Pd/NMC-700	34.3	6.7	23.3	28.7	7.1
Pd/NMC-800	27.7	2.8	22.7	36.2	10.6

Table S3. The ratio of each N species to total surface N in Pd/NMC-X.

Catalysts	Temperature (°C)	Additive	TOF (h <sup>-1</sup> )	Ref.
Pd/mpg-C <sub>3</sub> N <sub>4</sub>	25	no	144	[1]
AgPd/C	25	no	158	[2]
CoAuPd/C	25	no	49	[3]
Pd/CN + hv	25	no	64	[4]
PdAu/C	25	no	66	[5]
SBA-15-Amine/Pd	25	no	293	[6]
Pd <sub>SI</sub> /CNF	30	no	979	[7]
$Pd-Mn_x/SiO_2-NH_2$	50	no	1300	[8]
Pd/NMC-400	25	no	913	This work

Table S4. Comparison of TOF value of this work with previous reported ones.



Figure S1. (a) Nitrogen adsorption-desorption isotherms and (b) the pore-size distributions of NMC and MC samples.



Figure S2. Analysis result of the product composition for the catalytic formic acid decomposition on Pd/NMC-600 recorded on a GC-TCD with TDX-1 packed column.



Figure S3. Total gas generation profiles of FA decomposition catalyzed by supported Pd catalysts in 120 min reaction time. Reaction conditions: 10 ml of 1 M FA, Catalyst dosage: 30 mg, reaction temperature: 25 °C.

## Reference

[1] J.H. Lee, J. Ryu, J.Y. Kim, S.-W. Nam, J.H. Han, T.-H. Lim, S. Gautam, K.H. Chae, C.W. Yoon, Carbon dioxide mediated, reversible chemical hydrogen storage using a Pd nanocatalyst supported on mesoporous graphitic carbon nitride, *J. Mater. Chem. A* **2014**, *2* (25), 9490-9495.

[2] S. Zhang, O. Metin, D. Su, S. Sun, Monodisperse AgPd alloy nanoparticles and their superior catalysis for the dehydrogenation of formic acid, *Angew. Chem. Int. Ed.* **2013**, *125*, 3681-3684.

[3] Z.L. Wang, J.M. Yan, Y. Ping, H.L. Wang, W.T. Zheng, Q. Jiang, An efficient CoAuPd/C catalyst for hydrogen generation from formic acid at room temperature. *Angew. Chem. Int. Ed.* **2013**, *52*, 125 4502-4505.

[4] Y.Y. Cai, X.H. Li, Y.N. Zhang, X. Wei, K.-X. Wang, J.-S. Chen, Highly Efficient Dehydrogenation of Formic Acid over a Palladium-Nanoparticle-Based Mott-Schottky Photocatalyst, *Angew. Chem. Int. Ed.* **2013**, *125*, 12038-12041.

[5] Ö. Metin, X. Sun, S. Sun, Monodisperse gold–palladium alloy nanoparticles and their compositioncontrolled catalysis in formic acid dehydrogenation under mild conditions, *Nanoscale* **2013**, *5*, 910-912.

[6] K. Koh, J.E. Seo, J.H. Lee, A. Goswami, C.W. Yoon. T. Asefa, Ultrasmall palladium nanoparticles supported on amine-functionalized SBA-15 efficiently catalyze hydrogen evolution from formic acid, *J. Mater. Chem. A* **2014**, *2*, 20444-20449.

[7] F. Sanchez, D. Motta, L. Bocelli, S. Albonetti, A. Roldan, C. Hammond, A. Villa, N. Dimitratos, Investigation of the Catalytic Performance of Pd/CNFs for Hydrogen Evolution from Additive-Free Formic Acid Decomposition, *J. Carbon. Res.* **2018**, *4* (2), 26.

[8] A. Bulut, M. Yurderi, Y. Karatas, M. Zahmakiran, H. Kivrak, M. Gulcan, M. Kaya, Pd-MnO<sub>x</sub> nanoparticles dispersed on amine-grafted silica: highly efficient nanocatalyst for hydrogen production from additive-free dehydrogenation of formic acid under mild conditions, *Appl. Catal. B Environ.* 2015, *164*, 324-333.