Electronic Supplementary Information for

Three-dimensional Pd-Ag-S porous nanosponges for electrocatalytic nitrogen reduction to ammonia

Hongjing Wang, Songliang Liu, Hugang Zhang, Shuli Yin, You Xu, Xiaonian Li, Ziqiang Wang,* and Liang Wang*

State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China.

Corresponding authors' E-mails: zqwang@zjut.edu.cn; wangliang@zjut.edu.cn

Colorimetric detection of NO_3^-

The detection of NO_3^- was based on the reported literature.[1] The NO_3^- standard solution was prepared as follows (μg mL^{-1} corresponds to the concentration of NO_3^-).

1) 100.0 μg mL^{-1} stock: 0.1 g of pre-dried KNO_3 was added into 1.0 L of deionized water.

2) 5.0 μg mL^{-1} stock: 5.0 mL of the above 100 μg mL^{-1} stock was added in a 100.0 mL volumetric flask, and add deionized water to the scale mark.

3) 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 mL of 5.0 μg mL^{-1} stock solution were separately added into the test tube, to which the deionized water was then added to make up to 5.0 mL, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 μg mL^{-1} standard solutions were finally obtained.

UV-vis spectrophotometer measurement

Nitrates show typical absorption to ultraviolet light at the wavelength of 220 nm, in which the absorbance value is in proportion to the concentration of nitrates. Therefore, the content of the NO_3^- in Na_2SO_4 solution can be quantitatively determined. In a typical procedure, 5.0 mL of standard or sample solutions were added to the test tubes followed by addition of 0.10 mL of 1.0 M HCl. After shaking up and standing for 5 min, the concentration of NO_3^- was measured using UV-vis spectrophotometer at wavelength range from 200 nm to 300 nm. The standard curve NO_3^- determination was then plotted with the absorbance value difference at 220 nm and 275 nm as y axis and the concentration of NO_3^- as x axis.

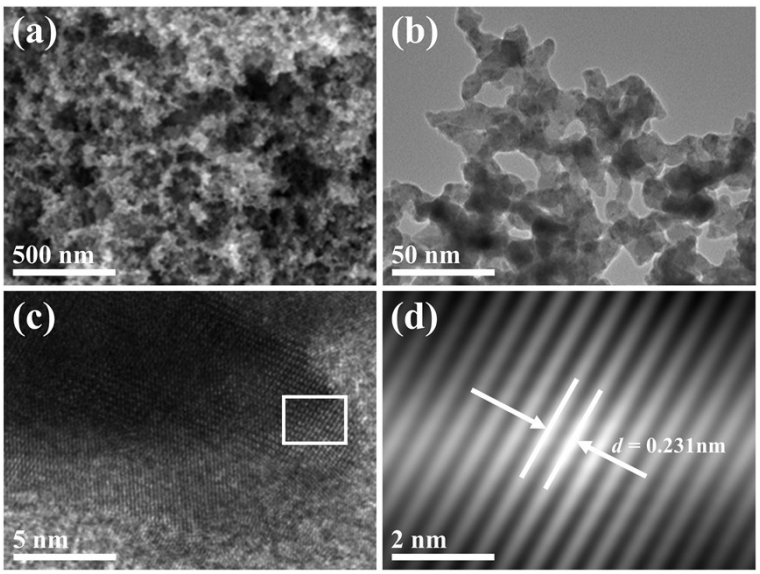

Fig. S1 (a) SEM, (b) TEM, and (c) HRTEM images of the 3D Pd-Ag PNSs. (d) The lattice fringes of the square area in (c).

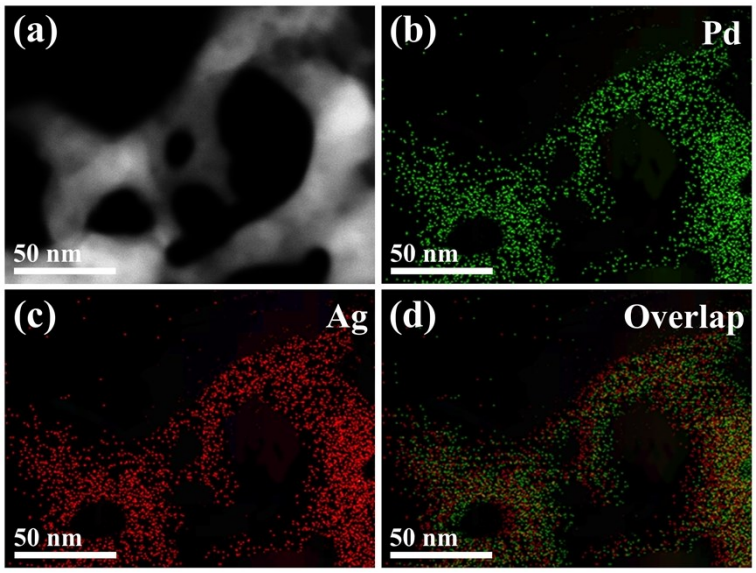

Fig. S2 (a) HAADF-STEM image and (b−d) elemental mapping images of the 3D Pd-Ag PNSs.

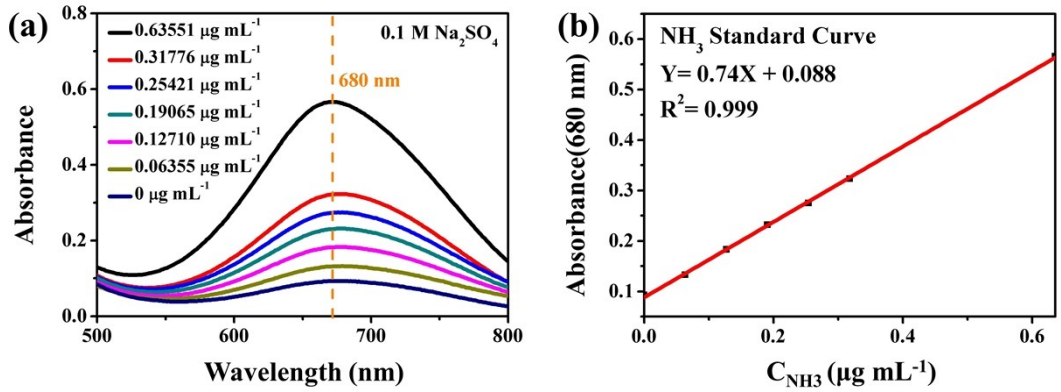

Fig. S3 The UV-Vis absorption spectra and corresponding calibration curves for the colorimetric NH_3 assay using the indophenol blue method in 0.1 M Na_2SO_4.

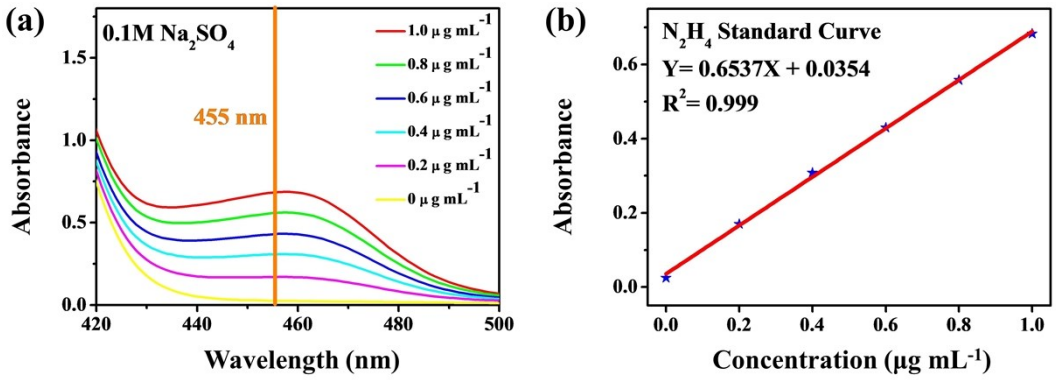

Fig. S4 (a) The UV-Vis absorption spectra and (b) corresponding calibration curve for the colorimetric N_2H_4 assay in 0.1 M Na_2SO_4.

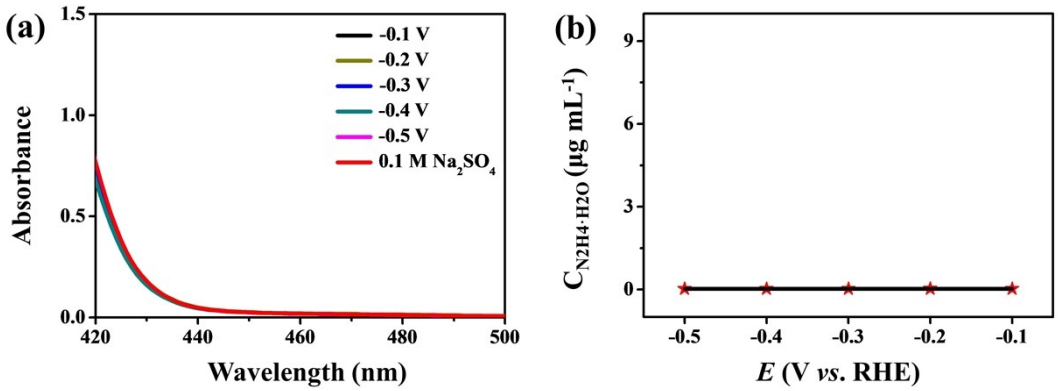

Fig. S5 (a) The UV-Vis absorption spectra and (b) corresponding yield rate of $N_2H_4 \cdot H_2O$ formation at selected potentials.

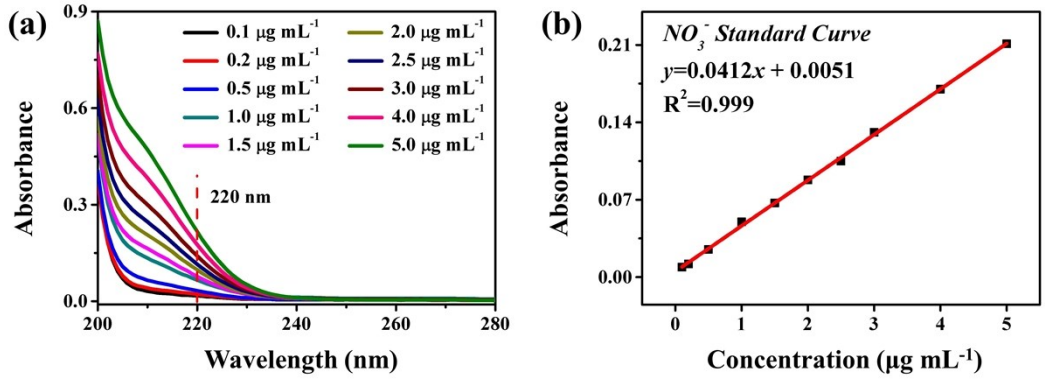

Fig. S6 Calibration for nitrate determination. (a) UV-vis spectra for various concentrations of KNO_3. (b) Calibration curve used for calculating the concentration of nitrate.

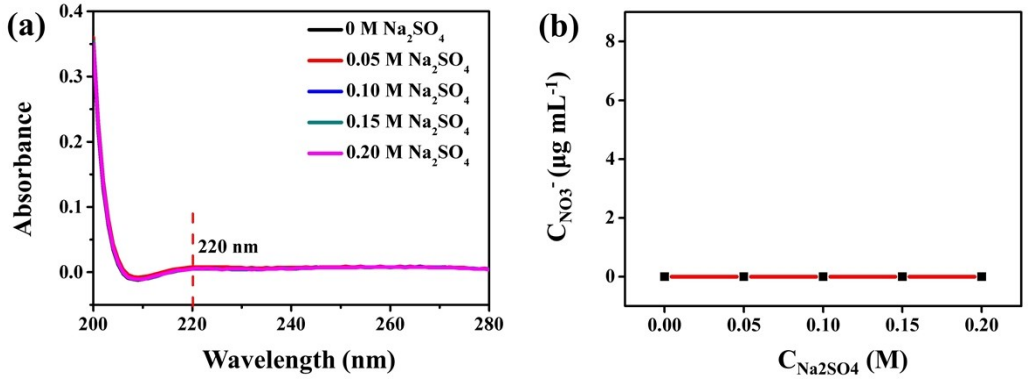

Fig. S7 (a) UV spectra for determining the concentration of NO_3^- in Na_2SO_4. (b)The concentration of NO_3^- in various concentrations of Na_2SO_4 .

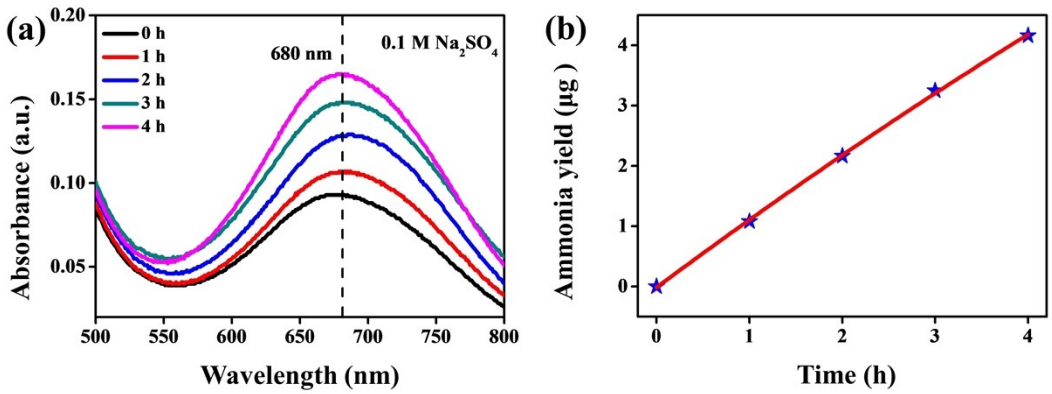

Fig. S8 (a) UV-vis absorption spectra of the electrolytes after electrolysis for different times, and (b) the relationship between the amount of ammonia formation and the electrolysis time.

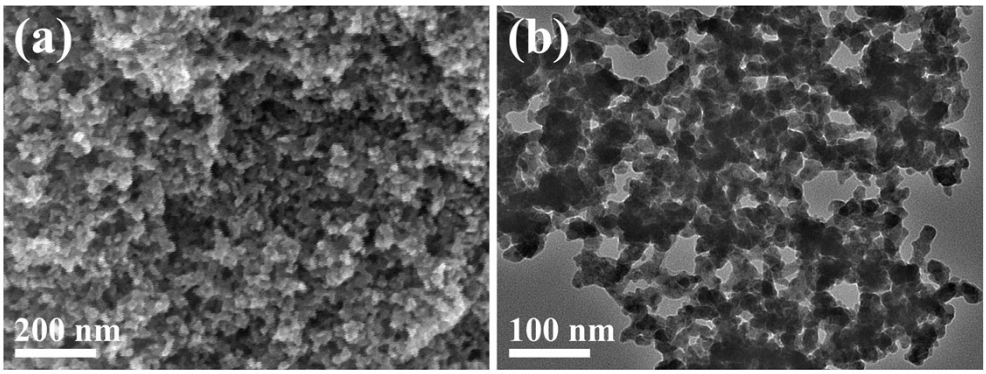

Fig. S9 (a) SEM and (b) TEM images of the 3D Pd-Ag-S PNSs after the durability test.

Table S1 Summary of the representative catalysts on electrocatalytic NRR at ambient conditions.

Catalysts	Electrolyte	NH_3 yield rate	FE (%)	Ref.
3D Pd-Ag-S PNSs	**0.1 M Na_2SO_4**	**9.73 μg h^{-1} $mg^{-1}_{cat.}$**	**18.41**	**This work**
Bi Nanoplates	0.2 M Na_2SO_4	5.45 μg h^{-1} $mg^{-1}_{Bi.}$	11.68	2
Pd/C	0.1 M PBS	4.50 μg h^{-1} $mg^{-1}_{cat.}$	8.20	3
Fe/Fe_3O_4	0.1 M PBS	0.19 μg h^{-1} cm^{-2}	8.29	4
Fe_3O_4/Ti	0.1 M Na_2SO_4	3.43 μg h^{-1} cm^{-2}	2.60	5
MoS_2/CC	0.1 M Na_2SO_4	4.94 μg h^{-1} cm^{-2}	1.17	6
Ag Film	0.1 M Na_2SO_4	1.27 μg h^{-1} cm^{-2}	7.36	7
V_2O_3/C	0.1 M Na_2SO_4	12.30 μg h^{-1} $mg^{-1}_{cat.}$	7.28	8
Fluorographene Nanosheets	0.1 M Na_2SO_4	9.30 μg h^{-1} $mg^{-1}_{cat.}$	4.20	9

References

1 L. Q. Li, C. Tang, D. Z. Yao, Y. Zheng and S.-Z. Qiao, *ACS Energy Lett*., 2019, **4**, 2111-2116.

2 Y. Wang, M. M. Shi, D. Bao, F. L. Meng, Q. Zhang, Y. T. Zhou, K. H. Liu, Y. Zhang, J. Z. Wang, Z. W. Chen, D. P. Liu, Z. Jiang, M. Luo, L. Gu, Q. H. Zhang, X. Z. Cao, Y. Yao, M. H. Shao, Y. Zhang, X. B. Zhang, J. G. Chen, J. M. Yan and Q. Jiang, *Angew. Chem., Int. Ed.,* 2019, **58**, 9464-9469.

3 J. Wang, L. Yu, L. Hu, G. Chen, H. Xin and X. Feng, *Nat. Commun.*, 2018, **9**, 1795.

4 L. Hu, A. Khaniya, J. Wang, G. Chen, W. E. Kaden and X. Feng, *ACS Catal.*, 2018, **8**, 9312-9319.

5 Q. Liu, X. Zhang, B. Zhang, Y. Luo, G. Cui, F. Xie and X. Sun, *Nanoscale*, 2018, **10**, 14386-14389.

6 L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.*, 2018, **30**, 1800191.

7 L. Ji, X. Shi, A. M. Asiri, B. Zheng and X. Sun, *Inorg. Chem.*, 2018, **57**, 14692-14697.

8 R. Zhang, J. Han, B. Zheng, X. Shi, A. M. Asiri and X. Sun, *Inorg. Chem. Front.*, 2019, **6**, 391-395.

9 J. Zhao, J. Yang, L. Ji, H. Wang, H. Chen, Z. Niu, Q. Liu, T. Li, G. Cui and X. Sun, *Chem. Commun.*, 2019, **55**, 4266-4269.