

Electronic Supplementary Information

**Nanoporous Silver by Pulsed Laser Deposition for High-Performance Oxygen Reduction Reaction and Hydrogen Peroxide Sensing**

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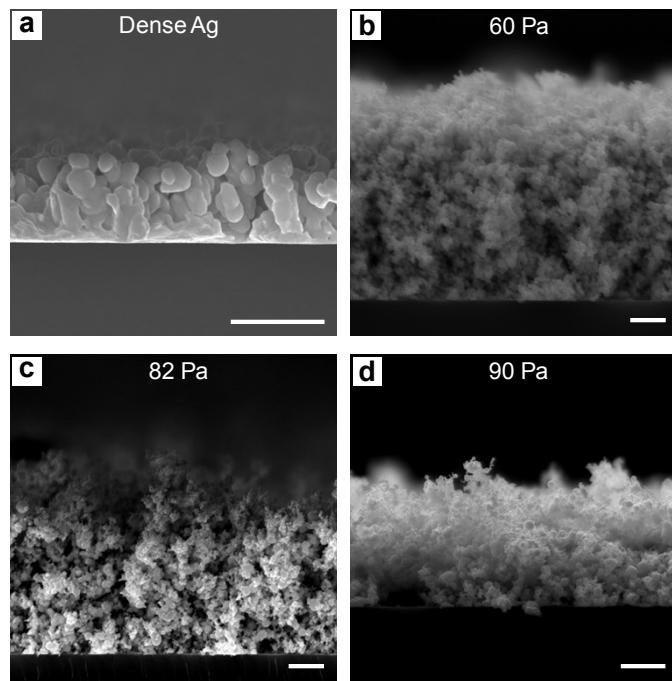
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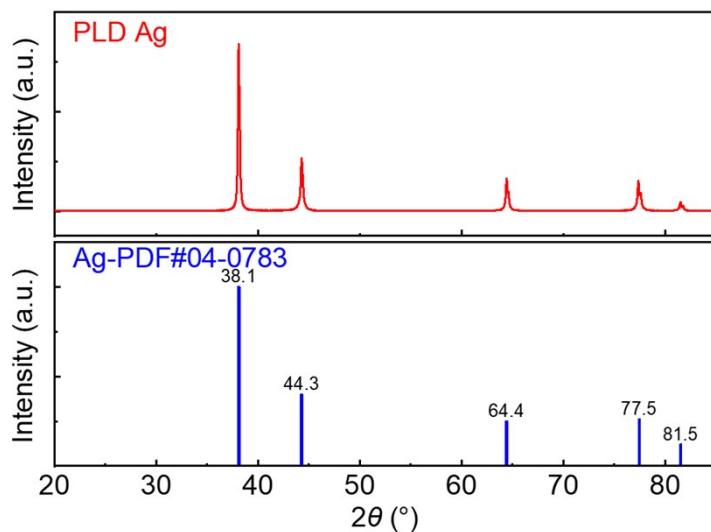
**Figure S1-S4**

**Table S1**

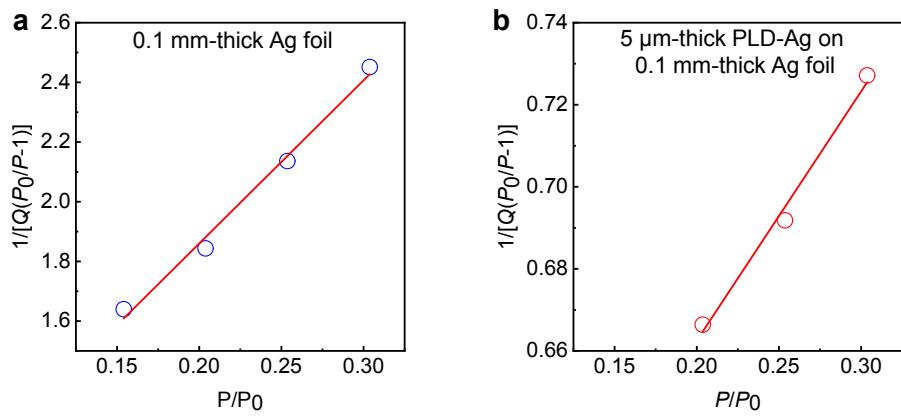
**References**



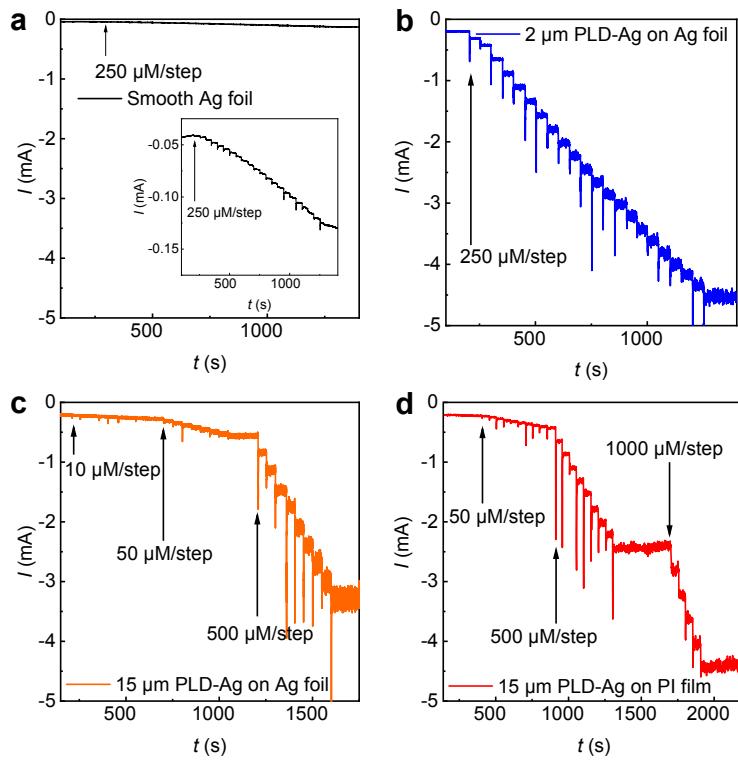
**Figure S1.** (a) SEM image of dense PLD-Ag. (b-d) SEM images of porous PLD-Ag deposited at different pressures of background gas: (b) 60 Pa; (c) 82 Pa; (d) 90 Pa (scale bars: 1  $\mu\text{m}$ ).



**Figure S2.** XRD spectrum of porous PLD-Ag (top) and standard XRD peaks of Ag (bottom).



**Figure S3.** BET measurement results and BET surface area of (a) 0.1 mm-thick smooth Ag foil (BET surface area:  $0.698 \text{ m}^2/\text{g}$ ) and (b) 5  $\mu\text{m}$ -thick PLD-Ag on 0.1 mm-thick smooth Ag foil (BET surface area:  $3.790 \text{ m}^2/\text{g}$ ).



**Figure S4.** Current-time curves of (a) smooth Ag foil, (b) 2- $\mu\text{m}$  porous PLD-Ag on Ag foil, (c) 15- $\mu\text{m}$  porous PLD-Ag on Ag foil and (d) 15- $\mu\text{m}$  porous PLD-Ag on PI film when certain amounts of  $\text{H}_2\text{O}_2$  were added into PBS at -0.2V (vs. SCE).

**Table S1.** ORR performance of some reported Ag-based catalysts.

Catalysts	$E_{\text{onset}}$	$E_{1/2}$	$n$	Electrolyte	Ref.
Nanoporous Ag	0.991 V <sub>RHE</sub>	0.880 V <sub>RHE</sub>	4	0.1 M KOH	[S1]
AgCl NWs	1.012 V <sub>RHE</sub>	0.84 V <sub>RHE</sub>	3.84	0.1 M NaOH	[S2]
Nanoporous Ag	1.014 V <sub>RHE</sub>	0.874 V <sub>RHE</sub>	4.0	0.1 M KOH	[S3]
Ag nanodendrites	0.98 V <sub>RHE</sub>	0.76 V <sub>RHE</sub>	3.9	0.1 M KOH	[S4]
Ag-MnO <sub>x</sub> /G	0.90 V <sub>RHE</sub>	0.72 V <sub>RHE</sub>	4.0	0.1 M KOH	[S5]
CuAg@Ag/NGS	0.94 V <sub>RHE</sub>	0.85 V <sub>RHE</sub>	3.6-3.8	0.1 M KOH	[S6]
Ag NW/C	0.904 V <sub>RHE</sub>	0.801 V <sub>RHE</sub>	4	0.1 M NaOH	[S7]
Ag NWs@NG	-0.05 V <sub>AgCl</sub>	-0.14 V <sub>AgCl</sub>	4	0.1 M KOH	[S8]
NCNTs-AgNFs	-0.1 V <sub>AgCl</sub>	-0.272 V <sub>AgCl</sub>	3.85	0.1 M KOH	[S9]
C-N/Ag-900-K	0.93 V <sub>RHE</sub>	0.71 V <sub>RHE</sub>	4.0	0.1 M KOH	[S10]
Ag-CeO <sub>2</sub>	0.905 V <sub>RHE</sub>	0.717 V <sub>RHE</sub>	3.46	0.1 M KOH	[S11]
Ag- Pr <sub>0.95</sub> Ba <sub>0.95</sub> Mn <sub>2</sub> O <sub>5+δ</sub> /C	0.92 V <sub>RHE</sub>	0.81 V <sub>RHE</sub>	4	0.1 M KOH	[S12]
HCT@HPC@Ag NPs	0.904 V <sub>RHE</sub>	0.754 V <sub>RHE</sub>	3.6-3.9	0.1 M KOH	[S13]
AgNCs/NG	-0.1 V <sub>AgCl</sub>	-0.25 V <sub>AgCl</sub>	3.55	0.1 M KOH	[S14]
Silver nanonet/graphene nano hybrid	0.924 V <sub>RHE</sub>	0.674 V <sub>RHE</sub>	4	0.1 M KOH	[S15]
rGO/MnO <sub>2</sub> /Ag	0.9 V <sub>RHE</sub>	0.732 V <sub>RHE</sub>	3.90	0.1 M KOH	[S16]
Ag-GNR	-0.133 V <sub>AgCl</sub>	-0.352 V <sub>AgCl</sub>	3.51	0.1 M KOH	[S17]
Ag/GO/C	0.826 V <sub>RHE</sub>	0.696 V <sub>RHE</sub>	/	0.1 M NaOH	[S18]
Porous PLD-Ag	1.007 V <sub>RHE</sub>	0.863 V <sub>RHE</sub>	3.9-4.0	0.1 M KOH	This Work

## References:

- S1. Zhao, W.; Huang, K.; Zhang, Q. H.; Wu, H.; Gu, L.; Yao, K. F.; Shen, Y.; Shao, Y., In-situ synthesis, operation and regeneration of nanoporous silver with high performance toward oxygen reduction reaction. *Nano Energy* 2019, 58, 69-77.
- S2. Kim, S. J.; Lee, S. C.; Lee, C.; Kim, M. H.; Lee, Y., Evolution of silver to a better electrocatalyst: Water-assisted oxygen reduction reaction at silver chloride nanowires in alkaline solution. *Nano Energy* 2018, 48, 134-143.
- S3. Xie, X.; Wei, M.; Du, L.; Nie, Y.; Qi, X.; Shao, Y.; Wei, Z., Enhancement in kinetics of the oxygen reduction on a silver catalyst by introduction of interlaces and defect-rich facets. *Journal of Materials Chemistry A* 2017, 5 (29), 15390-15394.
- S4. Chen, Z. Y.; Li, C. L.; Ni, Y. Y.; Kong, F. T.; Zhang, Y. B.; Kong, A. G.; Shan, Y. K., TCNQ-induced in-situ electrochemical deposition for the synthesis of silver nanodendrites as efficient bifunctional electrocatalysts. *Electrochim. Acta* 2017, 239, 45-55.
- S5. Shypunov, I.; Kongi, N.; Kozlova, J.; Matisen, L.; Ritslaid, P.; Sammelselg, V.; Tammeveski, K., Enhanced Oxygen Reduction Reaction Activity with Electrodeposited Ag on Manganese Oxide-Graphene Supported Electrocatalyst. *Electrocatalysis* 2015, 6 (5), 465-471.
- S6. Tran Duy, T.; Nguyen Dinh, C.; Hoa Van, H.; Kim, N. H.; Lee, J. H., CuAg@Ag Core-Shell Nanostructure Encapsulated by N-Doped Graphene as a High-Performance Catalyst for Oxygen Reduction Reaction. *ACS Applied Materials & Interfaces* 2018, 10 (5), 4672-4681.
- S7. Kim, S.-M.; Lee, S.-Y., The plasma-induced formation of silver nanocrystals in aqueous solution and their catalytic activity for oxygen reduction. *Nanotechnology* 2018, 29 (8).
- S8. Ji, D.; Wang, Y.; Chen, S.; Zhang, Y.; Li, L.; Ding, W.; Wei, Z., Nitrogen-doped graphene wrapped around silver nanowires for enhanced catalysis in oxygen reduction reaction. *Journal of Solid State Electrochemistry* 2018, 22 (7), 2287-2296.
- S9. Yasmin, S.; Ahmed, M. S.; Jeon, S., A noble silver nanoflower on nitrogen doped carbon nanotube for enhanced oxygen reduction reaction. *International Journal of Hydrogen Energy* 2017, 42 (2), 1075-1084.
- S10. Zhang, Z.; Li, H.; Hu, J.; Liu, B.; Zhang, Q.; Fernandez, C.; Peng, Q., High oxygen reduction reaction activity of C-N/Ag hybrid composites for Zn-air battery. *Journal of Alloys and Compounds* 2017, 694, 419-428.
- S11. Sun, S.; Xue, Y.; Wang, Q.; Li, S.; Huang, H.; Miao, H.; Liu, Z., Electrocatalytic activity of silver decorated ceria microspheres for the oxygen reduction reaction and their application in aluminium-air batteries. *Chem. Commun.* 2017, 53 (56), 7921-7924.
- S12. Zhang, Y.-Q.; Tao, H.-B.; Liu, J.; Sun, Y.-F.; Chen, J.; Hua, B.; Thundat, T.; Luo, J.-L., A rational design for enhanced oxygen reduction: Strongly coupled silver nanoparticles and engineered perovskite nanofibers. *Nano Energy* 2017, 38, 392-400.
- S13. Cao, C.; Wei, L.; Su, M.; Wang, G.; Shen, J., Template-free and one-pot synthesis of N-doped hollow carbon tube @ hierarchically porous carbon supporting homogeneous AgNPs for robust oxygen reduction catalyst. *Carbon* 2017, 112, 27-36.
- S14. Jin, S.; Chen, M.; Dong, H.; He, B.; Lu, H.; Su, L.; Dai, W.; Zhang, Q.; Zhang, X., Stable silver nanoclusters electrochemically deposited on nitrogen-doped graphene as efficient electrocatalyst for oxygen reduction reaction. *Journal of Power Sources* 2015, 274, 1173-1179.
- S15. Liu, R.; Yu, X.; Zhang, G.; Zhang, S.; Cao, H.; Dolbecq, A.; Mialane, P.; Keita, B.; Zhi, L., Polyoxometalate-mediated green synthesis of a 2D silver nanonet/graphene nanohybrid as

a synergistic catalyst for the oxygen reduction reaction. *Journal of Materials Chemistry A* 2013, 1 (38), 11961-11969.

S16. Lee, K., Ahmed, M. S., Jeon, S., Electrochemical deposition of silver on manganese dioxide coated reduced graphene oxide for enhanced oxygen reduction reaction. *Journal of Power Sources* 2015, 288, 261-269.

S17. Davis, D. J., Raji, A.-R. O., Lambert, T. N., Vigil, J. A., Li, L., Nan, K., Tour, J. M., Silver-Graphene Nanoribbon Composite Catalyst for the Oxygen Reduction Reaction in Alkaline Electrolyte. *Electroanalysis* 2014, 26 (1), 164-170.

S18. Yuan, L.; Jiang, L.; Liu, J., Xia, Z., Wang, S.; Sun, G., Facile synthesis of silver nanoparticles supported on three dimensional graphene oxide/carbon black composite and its application for oxygen reduction reaction. *Electrochim. Acta* 2014, 135, 168-174.