

Electronic Supplementary Information

Structural-Intensified PtCoRh Spiral Nanowires as Highly Active and Durable Electrocatalysts for Methanol Oxidation

Xiaowei Chen,^{a†} Wei Wang,^{a§†} Xuejiao Chen,^{*a} Xinyan Liao,^a Zixi Lyu,^a Kai Liu,^a and Shuifen Xie^{*a}

^aCollege of Materials Science and Engineering, Huaqiao University, Xiamen 361021, China

[§]Present Address: Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore

[†]These authors contribute equally to this work.

*Corresponding Author email: xjchen@hqu.edu.cn, or sfxie@hqu.edu.cn

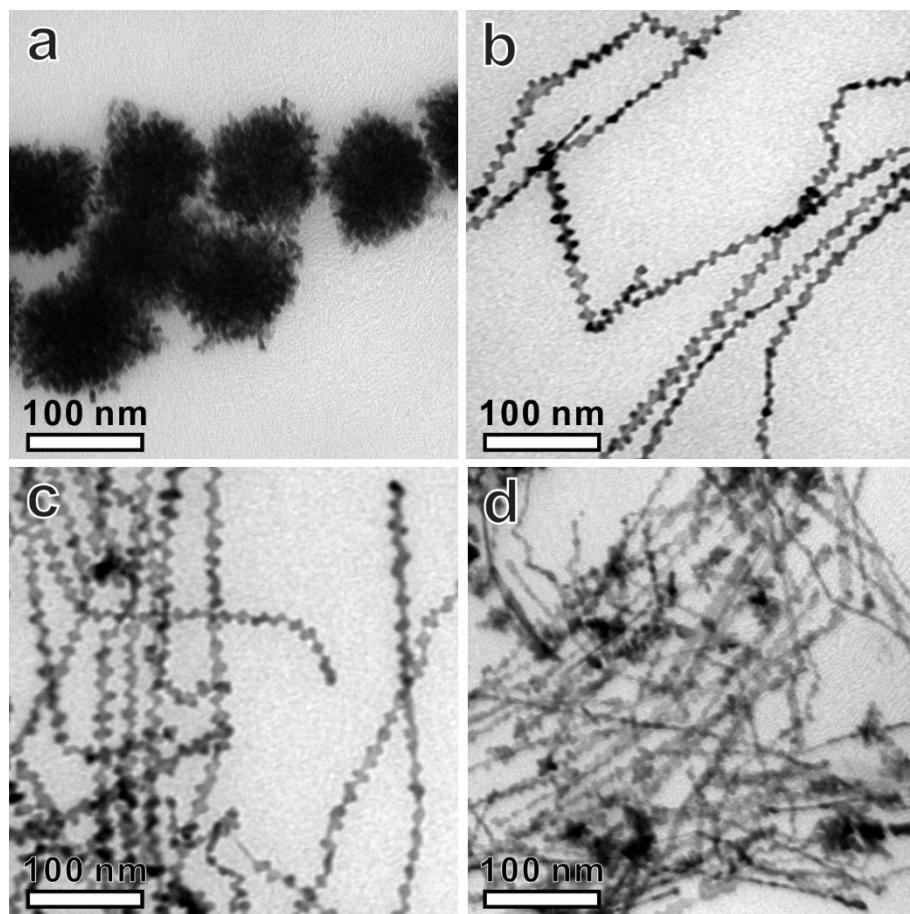


Figure S1. TEM images of the PtCoRh products obtained with different amounts of glucose:
(a) 0 mg; (b) 30 mg; (c) 60 mg; (d) 90 mg.

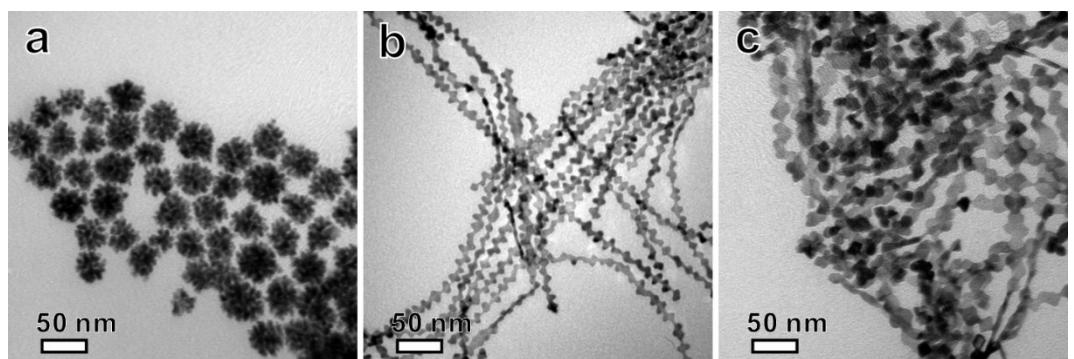


Figure S2. TEM images of the PtCoRh products obtained with different amounts of CTAC:
(a) 0 mg; (b) 32 mg; (c) 64 mg.

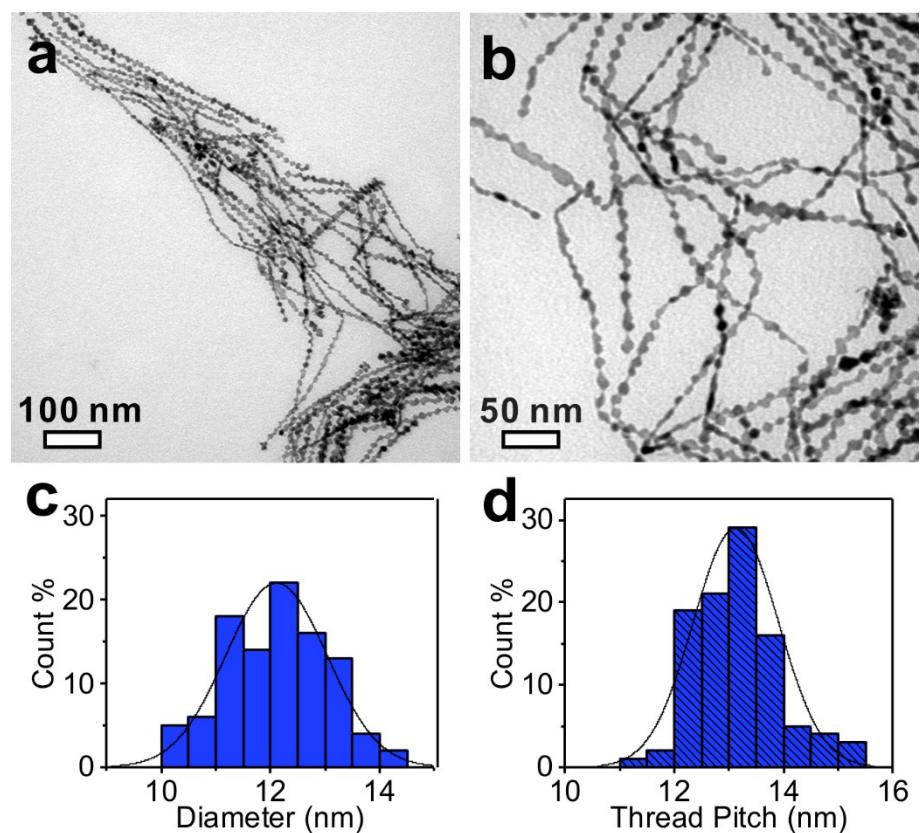


Figure S3. TEM images (a, b) and histogram of the statistical diameter (c) and thread pitch (d) distributions of the as-prepared Pt₈₅Co₁₅ SNWs.

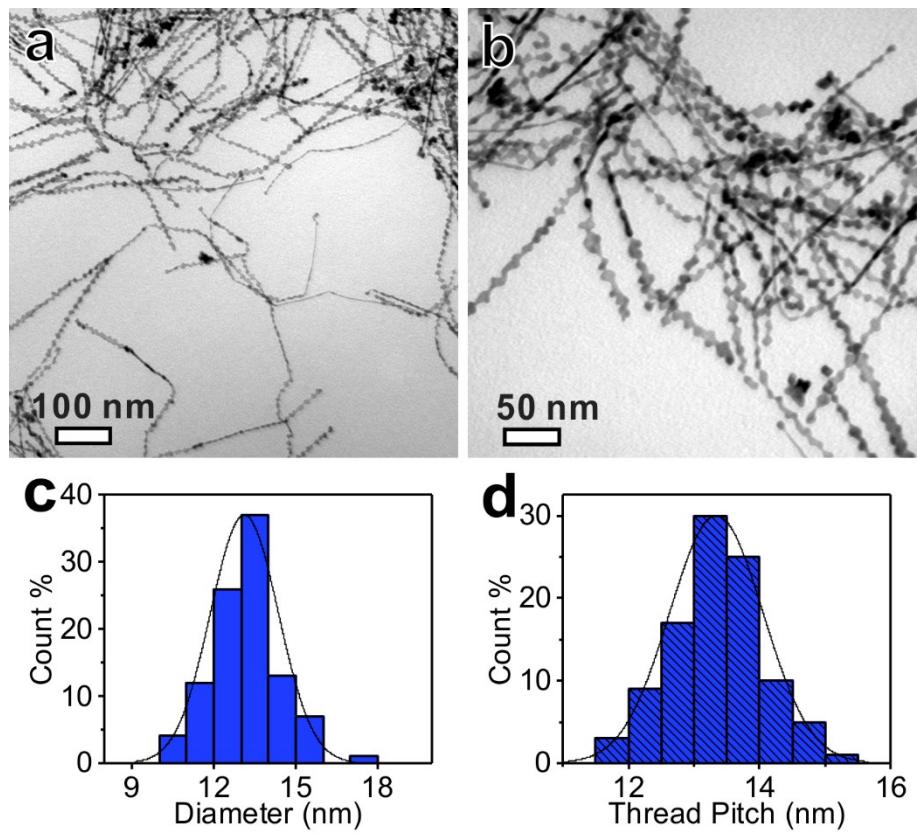


Figure S4. TEM images (a, b) and histogram of the statistical diameter (c) and thread pitch (d) distributions of the as-prepared $\text{Pt}_{85}\text{Co}_{10}\text{Rh}_5$ SNWs.

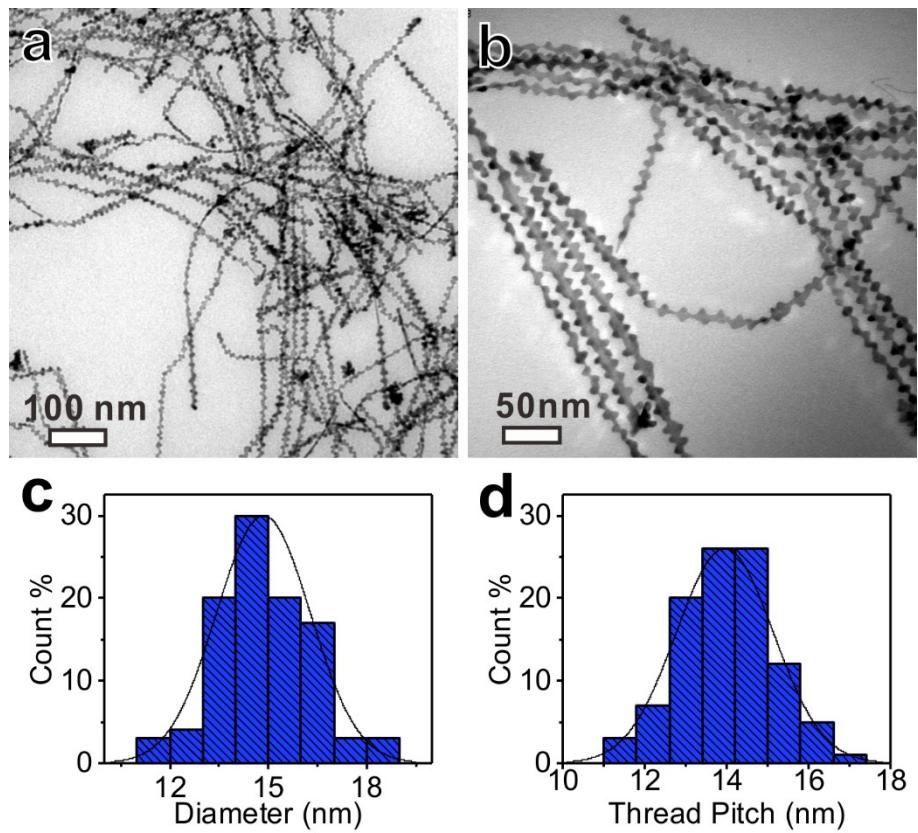


Figure S5. TEM images (a, b) and histogram of the statistical diameter (c) and thread pitch (d) distributions of the as-prepared Pt₇₇Co₁₁Rh₁₂ SNWs.

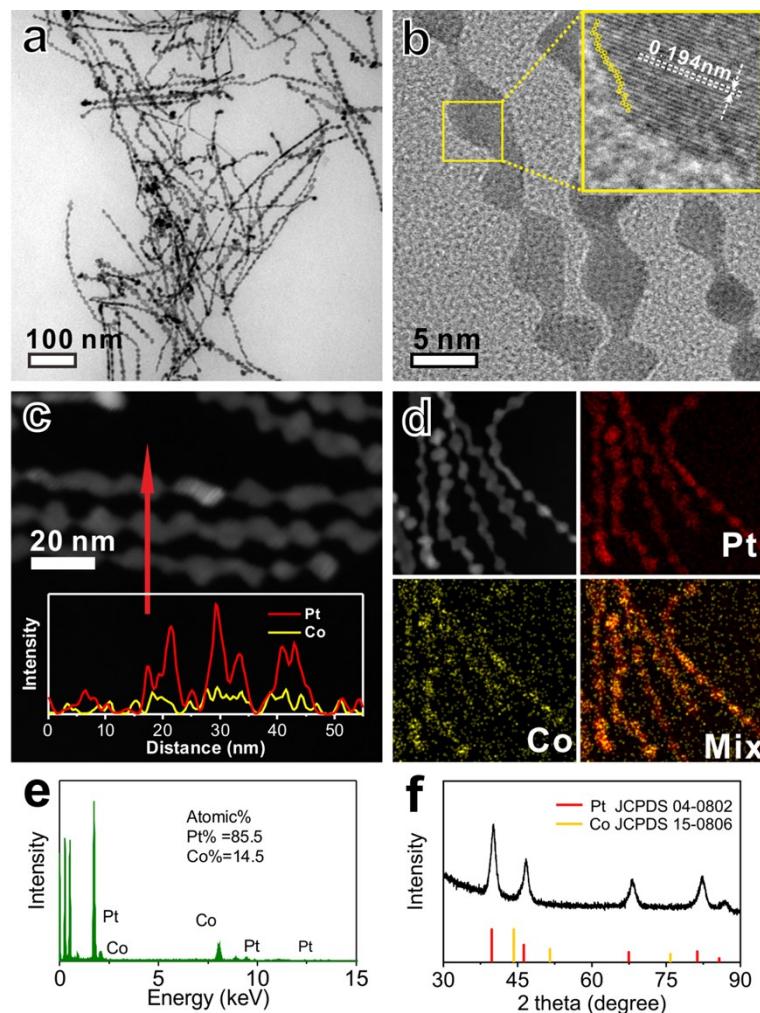


Figure S6. Structure and composition analysis of the $\text{Pt}_{85}\text{Co}_{15}$ SNWs. (a) TEM image; (b) HRTEM image; (c) STEM-EDS line-scanning profile; (d) STEM-EDS mapping; (e) SEM-EDS pattern; (f) PXRD pattern.

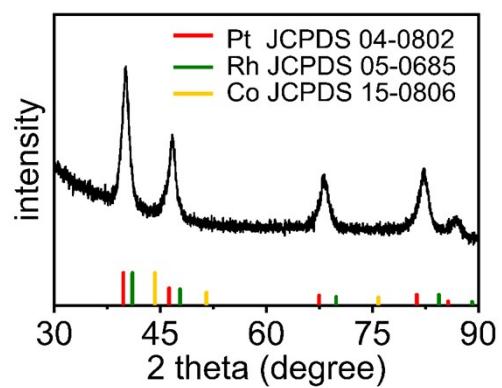


Figure S7. PXRD pattern of the as-prepared $\text{Pt}_{85}\text{Co}_{10}\text{Rh}_5$ SNWs.

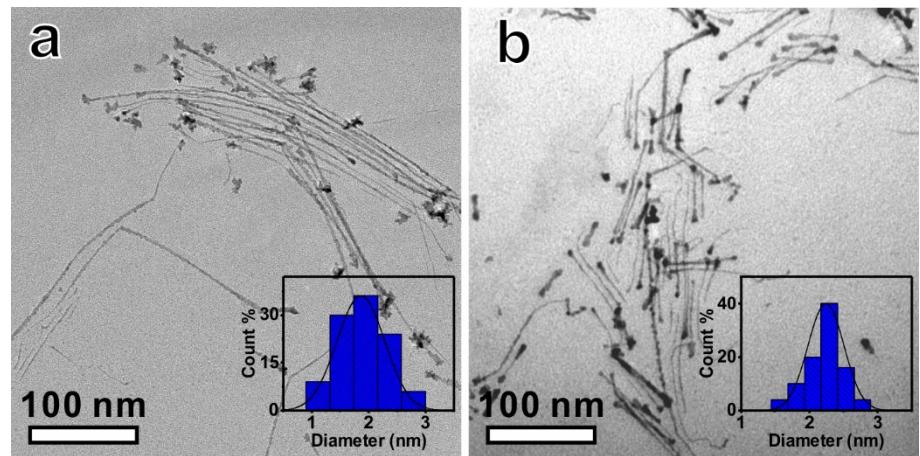


Figure S8. TEM images of the $\text{Pt}_{77}\text{Co}_{11}\text{Rh}_{12}$ SNWs intermediates obtained at different reaction times at 130 °C: (a) 1 h; (b) 3 h. The inserts are the size distribution histograms of the corresponding intermediates.

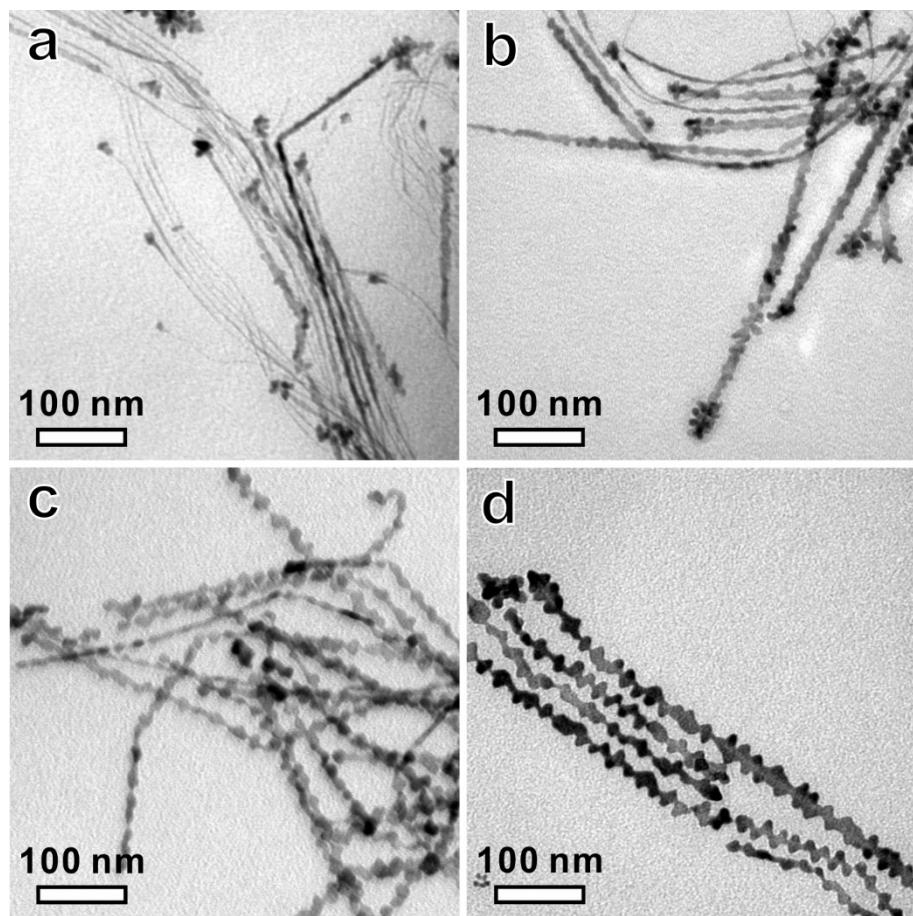


Figure S9. TEM images of the $\text{Pt}_{77}\text{Co}_{11}\text{Rh}_{12}$ SNWs intermediates obtained at different reaction times at 170 °C: (a) 1 min; (b) 1 h; (c) 3h; (d) 6 h.

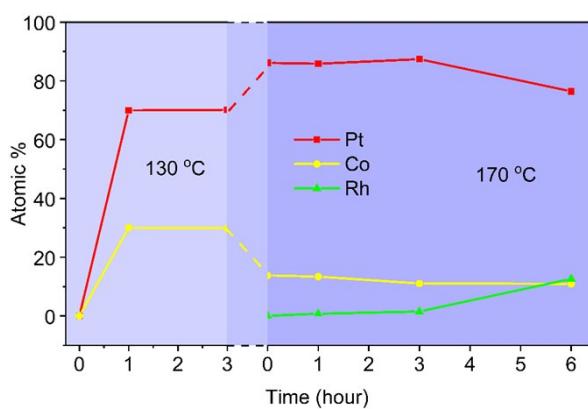


Figure S10. ICP-MS analyses of the Pt₇₇Co₁₁Rh₁₂ SNWs intermediates obtained at different reaction times.

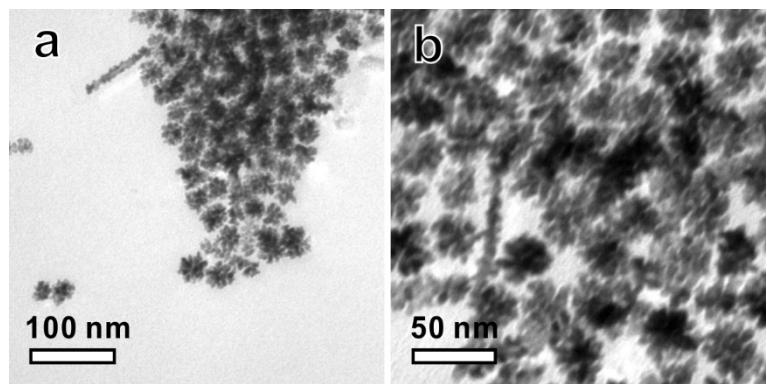


Figure S11. TEM of the PtCoRh nanodendrimer synthesized at 170 °C in a one-step approach with the same formula employed in synthesizing the Pt₇₇Co₁₁Rh₁₂ SNWs.

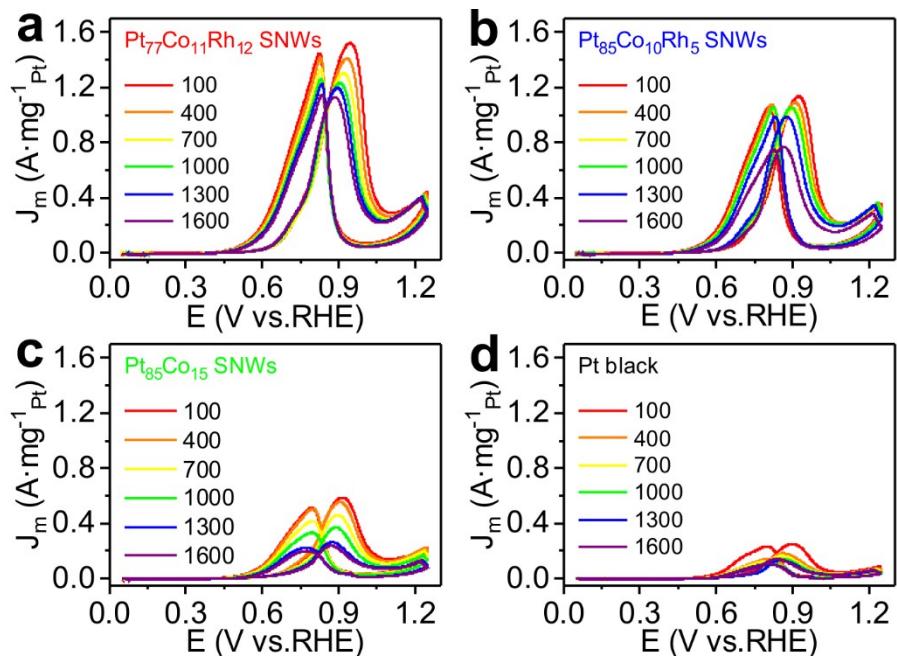


Figure S12. Selected MOR CV cycles of the (a) $\text{Pt}_{77}\text{Co}_{11}\text{Rh}_{12}$ SNWs, (b) $\text{Pt}_{85}\text{Co}_{10}\text{Rh}_5$ SNWs, (c) $\text{Pt}_{85}\text{Co}_{15}$ SNWs, and (d) Pt black.

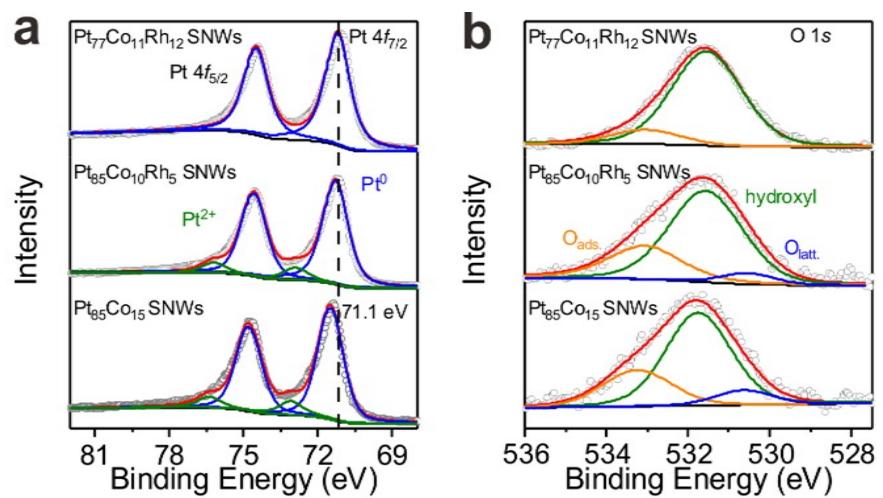


Figure S13. Pt 4f (a) and O 1s (b) XPS spectra of the Pt₇₇Co₁₁Rh₁₂ SNWs, Pt₈₅Co₁₀Rh₅ SNWs and Pt₈₅Co₁₅ SNWs, respectively.

Table S1. ECSAs of the Pt₇₇Co₁₁Rh₁₂, Pt₈₅Co₁₀Rh₅, Pt₈₅Co₁₅ SNWs and the Pt black.

| ECSA (m ² g ⁻¹ _{pt}) | Pt black | Pt ₈₅ Co ₁₅ SNWs | Pt ₈₅ Co ₁₀ Rh ₅ SNWs | Pt ₇₇ Co ₁₁ Rh ₁₂ SNWs |
|--|----------|--|--|---|
| H _{upd} | 14.4 | 25.4 | 29.4 | 31.4 |
| CO stripping | 12.9 | 23.1 | 27.2 | 35.7 |

Table S2. ICP-MS analyses of the Pt₈₅Co₁₅, Pt₈₅Co₁₀Rh₅, and Pt₇₇Co₁₁Rh₁₂ SNWs.

| Atomic % | Pt | Co | Rh |
|---|----|----|------|
| Pt ₈₅ Co ₁₅ SNWs | 85 | 15 | N.A. |
| Pt ₈₅ Co ₁₀ Rh ₅ SNWs | 85 | 10 | 5 |
| Pt ₇₇ Co ₁₁ Rh ₁₂ SNWs | 77 | 11 | 12 |

Table S3. Comparison of the recently reported Pt-based electrocatalysts for MOR in acidic media.

| Catalyst | Electrolyte Solution | MA | SA | Refs |
|--|--|-------------------------------|--------------------------------|------------------|
| Pt₇₇Co₁₁Rh₁₂SNWs | 0.1 M HClO₄+0.5 M methanol | 1.48 A mg⁻¹ | 4.76 mA cm⁻² | This work |
| Pt ₅₀ Au ₁₀ Cu ₄₀ NWs/C | 0.5 M H ₂ SO ₄ +1.0 M methanol | 0.928 A mg ⁻¹ | 0.88 mA cm ⁻² | 1 |
| Pt ₆₉ Ni ₁₆ Rh ₁₅ NWs/C | 0.1 M HClO ₄ +0.5 M methanol | 1.72 A mg ⁻¹ | 2.49 mA cm ⁻² | 2 |
| Pt NWs | - | ~0.5 A mg ⁻¹ | - | 3 |
| Pt ₃ Co NWs/C | 0.1 M HClO ₄ +0.2 M methanol | 1.02 A mg ⁻¹ | 1.95 mA cm ⁻² | 3 |
| Pt ₉₅ Co ₅ NWs | 0.5 M H ₂ SO ₄ +1.0 M methanol | 0.49 A mg ⁻¹ | 2.54 mA cm ⁻² | 4 |
| PtRu NWs | 0.1 M HClO ₄ +0.5 M methanol | 0.82 A mg ⁻¹ | 1.16 mA cm ⁻² | 5 |
| Pd ₇₃ Pt ₂₇ NWs | 0.5 M H ₂ SO ₄ +1.0 M methanol | 0.53 A mg ⁻¹ | - | 6 |
| Pt1Cu1-AA | 0.5 M H ₂ SO ₄ +1.0 M methanol | 2.252 A mg ⁻¹ | 6.09 mA cm ⁻² | 7 |
| Pt ₃ Co DENC/C | 0.5 M H ₂ SO ₄ +1.0 M methanol | ~0.66 A mg ⁻¹ | 4.14 mA cm ⁻² | 8 |
| PtNi CNCs | 0.5 M H ₂ SO ₄ +0.5 M methanol | ~0.68 A mg ⁻¹ | 1.37 mA cm ⁻² | 9 |

| | | | | |
|----------------------|---|-------------------------|--------------------------|----|
| Octahedron Pt–Ag NCs | 0.1 M HClO ₄ +0.5 M methanol | 0.73 A mg ⁻¹ | 6.61 mA cm ⁻² | 10 |
| TPH Pt NCs | 0.1 M HClO ₄ +1.0 M methanol | - | 8.1 mA cm ⁻² | 11 |

REFERENCES

- Y. Liu, G. Ren, M. Wang, Z. Zhang, Y. Liang, S. Wu and J. Shen, *J. Alloys Compd.*, 2019, **780**, 504-511.
- W. Zhang, Y. Yang, B. Huang, F. Lv, K. Wang, N. Li, M. Luo, Y. Chao, Y. Li, Y. Sun, Z. Xu, Y. Qin, W. Yang, J. Zhou, Y. Du, D. Su and S. Guo, *Adv. Mater.*, 2019, **31**, 1805833.
- L. Bu, S. Guo, X. Zhang, X. Shen, D. Su, G. Lu, X. Zhu, J. Yao, J. Guo and X. Huang, *Nat. Commun.*, 2016, **7**, 11850.
- Q. Lu, L. Sun, X. Zhao, J. Huang, C. Han and X. Yang, *Nano Res.*, 2018, **11**, 2562-2572.
- L. Huang, X. Zhang, Q. Wang, Y. Han, Y. Fang and S. Dong, *J. Am. Chem. Soc.*, 2018, **140**, 1142-1147.
- M. Rana, P. K. Patil, M. Chhetri, K. Dileep, R. Datta and U. K. Gautam, *J. Colloid Interface Sci.*, 2016, **463**, 99-106.
- H.-H. Li, Q.-Q. Fu, L. Xu, S.-Y. Ma, Y.-R. Zheng, X.-J. Liu and S.-H. Yu, *Energy Environ. Sci.*, 2017, **10**, 1751-1756.
- H. Du, S. Luo, K. Wang, M. Tang, R. Sriphathoorat, Y. Jin and P. K. Shen, *Chem. Mater.*, 2017, **29**, 9613-9617.
- P. Yang, X. Yuan, H. Hu, Y. Liu, H. Zheng, D. Yang, L. Chen, M. Cao, Y. Xu, Y. Min, Y. Li and Q. Zhang, *Adv. Funct. Mater.*, 2018, **28**, 1704774.
- J. Zhang, H. Li, J. Ye, Z. Cao, J. Chen, Q. Kuang, J. Zheng and Z. Xie, *Nano Energy*, 2019, **61**, 397-403.
- Y. Li, Y. Jiang, M. Chen, H. Liao, R. Huang, Z. Zhou, N. Tian, S. Chen, S. Sun, *Chem. Commun.*, 2012, **48**, 9531-9533.