Electronic Supplementary Information

The trimetallic AuAgPt nanowires for light-enhanced formic acid

electrolysis

Ze-Nong Zhang,^a Xiao-Hui Wang,^a Xin-Long Tian,^{*b} Yu Chen,^{*c} Shu-Ni Li,^{*a}

^{*a*} Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, PR China.

^b State Key Laboratory of Marine Resource Utilization in South China Sea, School of Chemical Engineering and Technology, Hainan University, Haikou, 570228, PR China

^c School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, PR China.

* Corresponding authors.

E-mail addresses: tianxl@hainanu.edu.cn (X. Tian), ndchenyu@gmail.com (Y. Chen), lishuni@snnu.edu.cn (S. Li)

Experimental section

Physical characterization

The chemical component, morphology, chemical state, crystallographic texture, surface area of electrocatalysts were characterized by high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM, Titan Cubed Themis G2 300), transmission electron microscopy (TEM, TECNAI G2 F20) with energy dispersive X-ray spectroscopy (EDX) accessory, scanning electron microscope (SEM, SU-8020), X-ray diffraction (XRD, DX-2700), and X-ray photoelectron spectroscopy (XPS, Kratos Analytical Ltd.). The ultraviolet-visible (UV–vis) measurements were carried out to observe the absorption of the sample by UV3600 instrument.

Electrochemical measurements

All electrochemical tests were performed at the CHI 760E electrochemical workstation using a three-electrode or two-electrode system. In the three-electrode system, the working electrode is a glassy carbon electrode, the reference electrode is a saturated calomel electrode, and the auxiliary electrode is a carbon rod. In the test system of light-enhanced FAOR, ITO glass was used as the working electrode. All potentials were about the reversible hydrogen electrode (RHE), where $E_{\text{RHE}} = E_{\text{SCE}} + 0.242 \text{ V} + 0.0591 \text{ pH}$. The ink was prepared by adding 2 mg of catalyst to a mixture solution of 0.8 mL of water, 0.2 mL of isopropanol, and 10 µL of Nafion. 4 µL of catalyst was uniformly coated on the working electrode and dried at room temperature. The catalyst loading on the working electrode was about 0.114 mg cm⁻².



Figure S1. (a) SEM image, (b) TEM image and the diameter distribution, (c) EDX pattern, (d) HAADF-STEM image and the corresponding EDX mapping of Au_{6.4}Ag_{3.6}-NWs.



Figure S2. XRD patterns of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs and $Au_{6.4}Ag_{3.6}$ -NWs.



Figure S3. HRTEM image and lattice spacings of Au_{6.4}Ag_{3.6}-NWs.



Figure S4. (a) SEM image, (b) EDX pattern of Au_{6.4}Ag_{2.7}Pt_{0.9}-NPs.



Figure S5. Metal normalized LSV curves of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs, $Au_{6.4}Ag_{2.7}Pt_{0.9}$ -NPs and Pt-NPs-C in N₂-purified 0.5 M H₂SO₄ + 0.5 M HCOOH solution at 50 mV s⁻¹.



Figure S6. CV curves of Au_{6.4}Ag_{2.6}Pt_{1.0}-NWs in N₂-purged 0.5 M H₂SO₄ electrolyte and 0.5 M H₂SO₄ + 0.5 M CH₃OH electrolyte at 50 mV s⁻¹, respectively.



Figure S7. The Pt percentage histogram of $Au_{6.4}Ag_{3.0}Pt_{0.6}$ -NWs, $Au_{6.4}Ag_{2.8}Pt_{0.8}$ -NWs, $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs, $Au_{6.4}Ag_{2.4}Pt_{1.2}$ -NWs, and $Au_{6.4}Ag_{2.0}Pt_{1.6}$ -NWs obtained by XPS and EDX. The Pt atomic contents of AuAgPt-NWs were analyzed by EDX and XPS. The results show that the Pt contents of the two measurement methods are almost close to each other, thus confirming that their alloy property.



Figure S8. TEM images of $Au_{6.4}Ag_{3.0}Pt_{0.6}$ -NWs, $Au_{6.4}Ag_{2.8}Pt_{0.8}$ -NWs, $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs, $Au_{6.4}Ag_{2.4}Pt_{1.2}$ -NWs, and $Au_{6.4}Ag_{2.0}Pt_{1.6}$ -NWs, respectively.



Figure S9. TEM image of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs after chronoamperometry test.



Figure S10. EDX pattern of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs after chronoamperometry test.



Figure S11. Pt foil (1×1 cm²) was selected as both the working electrode and counter electrode and Hg/HgCl₂ electrode was selected as reference electrode. LSV was carried out at a scan rate of 5 mV·s⁻¹. As shown in Figure S11, the zero current point is at about -0.284 V in 0.5 M H₂SO₄, so $E_{RHE} = E_{Hg/HgCl_2} + 0.284$ V. The actual pH value of the electrolyte (0.5 M H₂SO₄) measured by the pH meter is 0.69. Therefore, the potential of the used Hg/HgCl₂ electrode is ~-0.282 V, which is very close to the standard potential (-0.284 V, Hg/HgCl₂ in 0.5 M H₂SO₄).



Figure S12. Nyquist plots of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs, $Au_{6.4}Ag_{2.7}Pt_{0.9}$ -NPs, Pt-NPs-C, and $Au_{6.4}Ag_{3.6}$ -NWs in 0.5 M H₂SO₄ electrolyte.



Figure S13. LSV curves of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs in N₂-purged 0.5 M H₂SO₄ electrolyte and 0.5 M H₂SO₄ + 0.5 M HCOOH electrolyte at 5 mV s⁻¹, respectively.



Figure S14. LSV curves of the $Au_{6.4}Ag_{2.7}Pt_{0.9}$ -NPs in 0.5 M H₂SO₄ + 0.5 M HCOOH solution at 50 mV s⁻¹ with and without light excitation.



Figure S15. Chronoamperometric curves of the $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs in 0.5 M H₂SO₄ + 0.5 M HCOOH electrolyte under alternating light and dark conditions.



Figure S16. The surface temperature of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs was measured under xenon lamp irradiation conditions using infrared thermometry.



Figure S17. LSV curves of the $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs in 0.5 M H₂SO₄ + 0.5 M HCOOH electrolyte with and without 808 nm laser irradiation.



Figure S18. LSV curves of the $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs in 0.5 M H₂SO₄ + 0.5 M HCOOH electrolyte with and without 980 nm laser irradiation.



Figure S19. LSV curves of $Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs in N₂-purged 0.5 M H₂SO₄ electrolyte at 5 mV s⁻¹ with and without light excitation.

Catalyst	Electrolyte	η ₁₀ / mV	Tafel Slope / mV dec ⁻¹	Ref.
$Au_{6.4}Ag_{2.6}Pt_{1.0}$ -NWs	0.5 M H ₂ SO ₄	16.4	34.8	This work
Vanadium carbide MXene with atomic Pt confinement	$0.5 \mathrm{~M~H_2SO_4}$	27	36.5	20221
Pt@Mn-SAs/ N-doped carbon	$0.5 \text{ M} \text{H}_2\text{SO}_4$	25	30.7	2023 ²
PtZn alloy on N-doped carbon	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	29	52	2022 ³
Pt-based NiCo alloy NPs modified with Mo	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	90	45.4	20224
Pt@Co SAs-ZIF-porous nitrogen- doped carbon matrix	0.5 M H ₂ SO ₄	27	21	20215
Highly dispersed Pt with the defective carbon sheet surface	$0.5 \text{ M H}_2 \text{SO}_4$	25	30	20216
MoS ₂ nanosheets supported single atoms Pt	$0.5 \text{ M H}_2 \text{SO}_4$	88.4	55.7	20227
Vanadium carbide nanosheets supported Pt nanoparticles	$0.5 \text{ M H}_2\text{SO}_4$	24	33	20228

Table S1. HER activity of various reported Pt-based electrocatalysts in]	H_2SO_4 electrolyte.
---	------------------------

- S. Park, Y.-L. Lee, Y. Yoon, S.Y. Park, S. Yim, W. Song, S. Myung, K.-S. Lee, H. Chang, S.S. Lee, K.-S. An, *Appl. Catal. B-Environ.*, 2022, **304**, 120989.
- L. Gong, J. Zhu, F. Xia, Y. Zhang, W. Shi, L. Chen, J. Yu, J. Wu, S. Mu, ACS Catal., 2023, 13, 4012-4020.
- W. Yan, S. Cao, H. Liu, Q. Xing, J. Ren, Z. Li, X. Li, X. Lu, Y. Chen, ACS Appl. Energy Mater., 2022, 5, 13791-13801.
- G.M. Leteba, D.R.G. Mitchell, L. Macheli, P.B.J. Levecque, B.P. Doyle, E. van Steen, C.I. Lang, ACS Appl. Energy Mater., 2022, 5, 15102-15113.
- L. Liang, H. Jin, H. Zhou, B. Liu, C. Hu, D. Chen, Z. Wang, Z. Hu, Y. Zhao, H.-W. Li, D. He, S. Mu, *Nano Energy*, 2021, 88, 106221.
- 6. W. Quan, X. Ruan, Y. Lin, J. Luo, Y. Huang, Nanoscale, 2021, 13, 18677-18683.
- 7. J. Zhu, Y. Tu, L. Cai, H. Ma, Y. Chai, L. Zhang, W. Zhang, Small, 2022, 18, e2104824.
- 8. N. Wang, X. Bo, M. Zhou, ACS Appl. Mater. Interfaces, 2022, 14, 23332-23341.