Supplementary Information (SI) for Dalton Transactions.

Supporting Information

Synergizing Ag Alloying and Urchin-Like Structure on Steering Formic Acid Oxidation Toward the Direct Pathway in Acidic Medium

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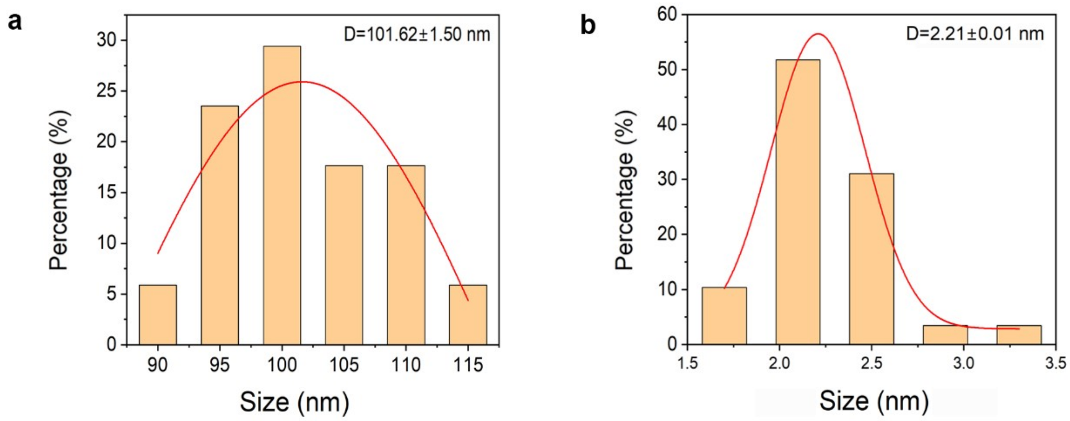

Figure S1. Size distribution histograms for (a) overall particles and (b) branches.

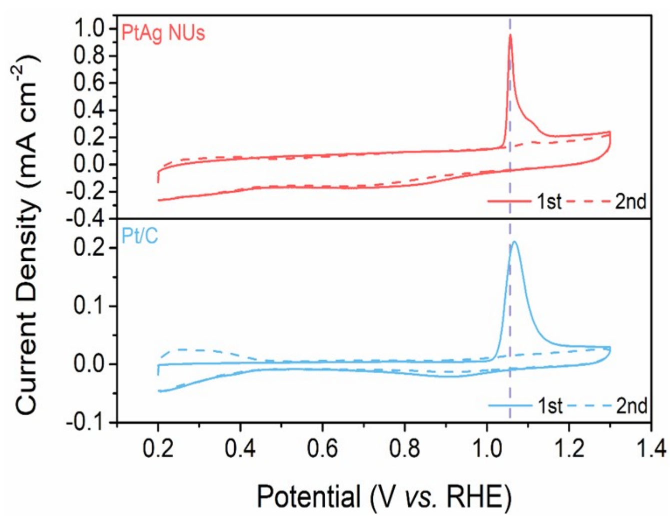

Figure S2. CO stripping voltammograms collected in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

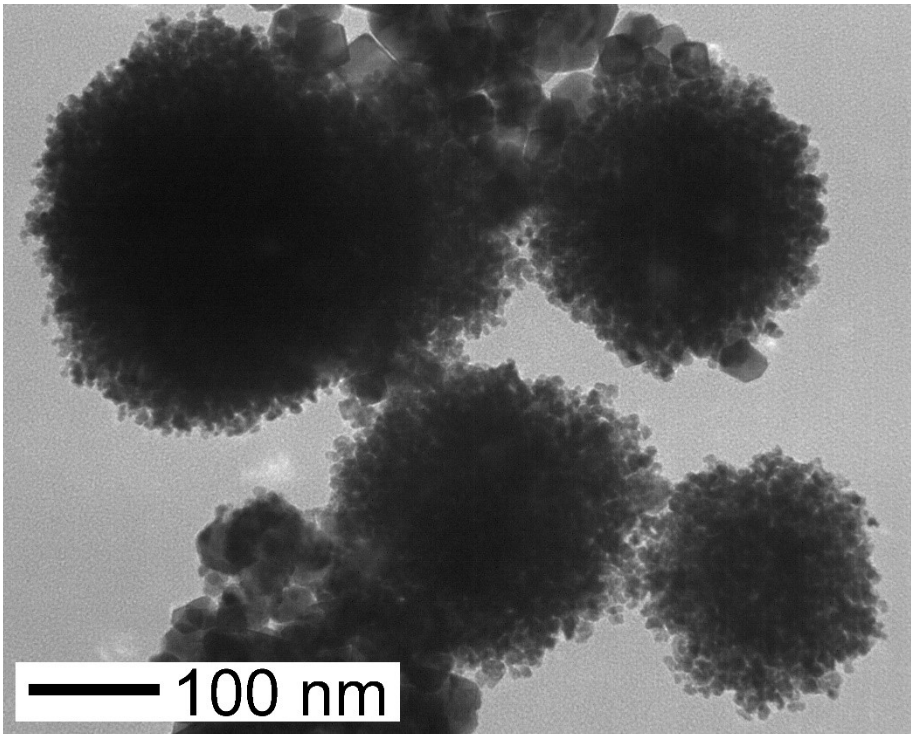

Figure S3. TEM image of PtAg NUs after the CA test.

Table S1. Summary of the relative peak area (%) for each split B.E. peak and the parameters used to fit the Ag(I), Ag(0), and Pt(II), Pt(0) high-reesolution XPS spectra of PtAg NUs.

Element	B. E. Peak (eV)	FWHM (eV)	Peak Area (%)	Element /Oxidation state
Pt	70.5	0.83	25.59	Pt (0)
	71.0	1.76	27.90	Pt (II)
	73.9	0.99	26.14	Pt (0)
	74.5	2.48	20.38	Pt (II)
Ag	367.3	1.00	52.62	Ag (0)
	368.6	0.92	6.81	Ag (I)
	373.1	0.84	33.57	Ag (0)
	374.1	0.92	7.00	Ag (I)

Table S2. XRD results and theoretical diffraction peak positions of as-prepared of PtAg NUs (Pt:Ag=86.17:13.83)

Sample/Element	**Value Source**	**Diffraction Peak Position (°)**			
		(111)	**(200)**	**(220)**	**(311)**
PtAg NUs	XRD	38.8	45.1	65.8	79.4
	Theoretical*	39.2	45.8	66.7	80.3
Pt	JCPDS No. 004-0802	39.5	46.0	67.0	80.7
Ag	JCPDS No. 004-0783	38.2	44.5	64.7	77.7

Table S3. Summary of FAOR performances of PtAg NUs/C electrocatalysts in the present study. Data of commercial Pt/C was provided for comparison.

Electrocatalyst	E_s** (mV)	*E_{p1} (mV)	*E_{p2} (mV)	ECSA (m^2 g^{-1})	*i_r/i_{f1}	*i_r/i_{f2}	*SA_1 (mA cm^{-2})	*SA_2 (mA cm^{-2})	i (t=3600s) (mA cm^{-2})
PtAg NUs/C	320.0	682.9	1059.9	2.6	1.35	1.78	0.88	0.66	0.035
Pt/C	430.0	715.1	1090.5	58.0	8.0	2.35	0.05	0.17	0.006

* E_{p1} and E_{p2} correspond to the potentials of two pathways for formic acid oxidation catalyzed by the sample, respectively; I_r/i_{f1} and i_r/i_{f2} correspond to E_{p1} and E_{p2}, respectively; *SA_1 and *SA_2 correspond to E_{p1} and E_{p2}, respective

** E_s corresponds to onset potential, which was determined using the linear extrapolation method. Specifically, the linear region of the rising current portion of the polarization curve was extrapolated to intersect with the baseline current region, and the potential at this intersection point was taken as the onset potential. This approach was consistently applied across all samples to ensure a standardized and objective comparison.

Table S4. Comparison of the specific activity of PtAg NUs/C with recently reported Pt-based and PtAg-based electrocatalysts for the formic acid oxidation reaction.

Electrocatalyst	SA_1	SA_2	SA_1/SA_2	Enhancement factor	Ref.
PtAg NUs/C	0.88	0.66	1.33	17.6	current work
Pt_{10}%/Sb (Antimonene)	0.95	0.12	7.92	2.02	[1]
Pt_{20}%/Sb (Antimonene)	2.15	0.7	3.07	4.57	[1]
Pt_{40}%/Sb (Antimonene)	1.74	0.57	3.05	3.7	[1]
Pt-C_3N_4@CNT	0.79	0.08	9.88	2.55	[2]
PtNi/Nifoam	0.62	0.06	10.33	1.77	[3]
NiO_x/Pt	9	1.2	7.5	2	[4]
FeO_x/NiO_x/Pt	22	2	11	4.89	[4]
a-FeO_x/NiO_x/Pt	28	1.7	16.5	6.22	[4]
Pt Islands on 3D Nut-like PtAg Nanocrystals	3.31	-	-	7.36	[5]
N-doped Graphene Supported Hollow PtAg Nanodendrites	6.14	-	-	11.81	[6]
Pt_1Co_1 Alloy/C	6.71	-	-	14.91	[7]
Pt_2–$PtTe_2$ Heterojunction Nanosheet Assemblies/C	8.4	-	-	18.67	[8]

References

[1] Y. Zhang, M. Qiao, Y. Huang, Y. Zou, Z. Liu, L. Tao, Y. Li, C.-L. Dong and S. Wang, *Research*, 2020, **2020**.

[2] C. Li, Z. Tang, L. Shi, Y. Li, Y. Ji, K. Zhang, Z. Yang and Y.-M. Yan, *Chemistry*, 2023, **5**, 1621-1633.

[3] A. Nacys, D. Simkunaitė, A. Balciunaite, A. Zabielaite, D. Upskuviene, R. Levinas, V. Jasulaitiene, V. Kovalevskij, B. Simkunaite-Stanyniene, L. Tamasauskaite-Tamasiunaite and E. Norkus, *Materials*, 2023, **16**, 6427.

[4] B. A. Al-Qodami, H. H. Alalawy, S. Y. Sayed, I. M. Al-Akraa, N. K. Allam and A. M. Mohammad, *RSC Adv.*, 2022, **12**, 20395-20402.

[5] H. Xu, P. Song, B. Yan, J. Wang, C. Wang, Y. Shiraishi, P. Yang and Y. Du, *ChemSusChem*, 2018, **11**, 1056-1062.

[6] H. Xu, B. Yan, S. Li, J. Wang, C. Wang, J. Guo and Y. Du, *ACS Sustain. Chem. Eng.*, 2018, **6**, 609-617.

[7] Z. Zheng, B. Liu, J. Qiu, S. Xu, Y. Wang, M. Zhang, K. Li, Z. Sun, Z. Li, Y. Wan, C. R. A. Catlow and K. Yan, *ACS Catal.*, 2024, **14**, 18333-18344.

[8] C. Dong, B. Zhang, H. Song, S. Zhou, J. Ye, H.-G. Liao, L. Dong, X. Huang and L. Bu, *ACS Nano*, 2024, **18**, 10008-10018.