

Supporting Information

Photo-Assisted Synthesis of Au@PtAu Core-Shell Nanoparticles with Controllable Surface Composition for Methanol Electro-oxidation

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Table S1. Some reported mass activities of free-standing Pt-Au bimetallic nanomaterials for methanol electro-oxidation

Materials	Electrolytes	Mass activities (A mg ⁻¹ Pt)	References
Pt-Au	0.5M CH ₃ OH+0.1M HClO ₄ 50mV/s	0.8	[1]
Au@PtAu_{0.5}	1M CH₃OH+0.1M HClO₄ 50mV/s	0.76	Our work
Au ₃₀ -Pt _{array}	1M CH ₃ OH+0.5M H ₂ SO ₄	0.66	[2]
Pt-Au	1M CH ₃ OH+1M HClO ₄	0.625	[3]
Au-Pt alloyed nanowire	1M CH ₃ OH+0.5M H ₂ SO ₄ 50mV/s	0.58	[4]
Au-Pt core-rods	0.5M CH ₃ OH+0.5M H ₂ SO ₄	0.561	[5]
Au@Pt (Pt ₅ Au)	1M CH ₃ OH+0.5M H ₂ SO ₄ 20mV/s	0.45	[6]
Pt-on-Au	1M CH ₃ OH+0.5M H ₂ SO ₄ 50mV/s	~0.43	[7]
Pt _{0.81} Au _{0.19} alloy core-Pt shell	2M CH ₃ OH+0.1M H ₂ SO ₄	0.426	[8]
Pt-Au	?CH ₃ OH+0.1M HClO ₄	~0.38	[9]
Pt-Au alloy	0.5M CH ₃ OH+0.5M H ₂ SO ₄ 50mV/s	0.348	[10]
Au-Pt nanowire	1M CH ₃ OH+0.1M HClO ₄	~0.34	[11]
Au@Pt	2M CH ₃ OH+0.5M H ₂ SO ₄ 50mV/s	0.149	[12]
Au@Pt	0.5M CH ₃ OH+0.5M H ₂ SO ₄ 50mV/s	~0.115	[13]

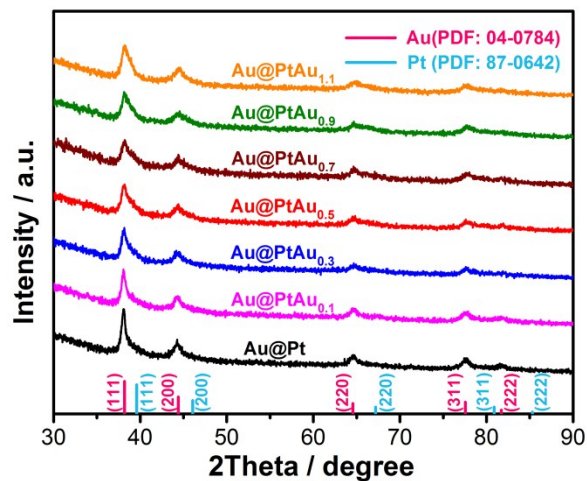


Fig. S1 The XRD patterns of the as-prepared Au@PtAu_m NPs, with m: 0-1.1.

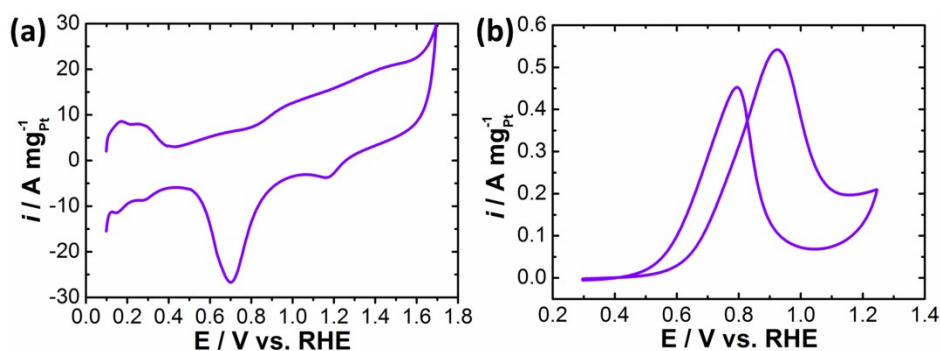


Fig. S2 The cyclic voltammetry curve (a) and current density (b) toward methanol electro-oxidation in 0.1M HClO₄ of Au@PtAu_{0.5} NPs prepared without photo-irradiation. The scan rates are 100mV/s and 50mV/s, respectively.

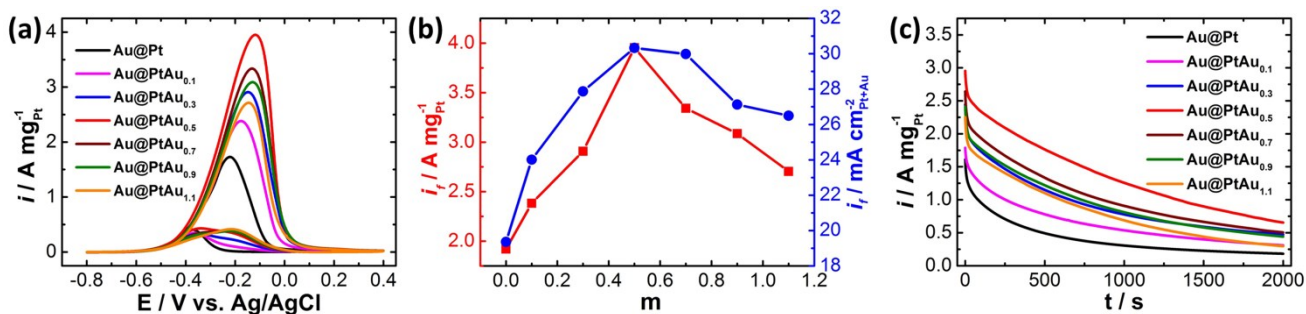


Fig. S3 Activity, durability and activity variation trend of Au@PtAu_m NPs toward methanol electro-oxidation. (a) Current densities of Au@PtAu_m NPs toward methanol electro-oxidation in 1M KOH at 50mV/s. (b) Catalytic activities (corresponding to the peak current densities) variation trend of the as-prepared Au@PtAu_m NPs normalized either by Pt mass (red curve) or EASA of Pt and Au (blue curve). (c) Long term current-time curves measured in 1M KOH+1M CH₃OH at -0.2V vs. Ag/AgCl.

REFERENCES

- [1] H. J. You, F. L. Zhang, Z. Liu and J. X. Fang, *ACS Catal.*, 2014, **4**, 2829-2835.
- [2] M. Y. Duan, R. Liang, N. Tian, Y. J. Li and E. S. Yeung, *Electrochim Acta*, 2013, **87**, 432-437.
- [3] Z. H. Zhang, Y. Wang and X. G. Wang, *Nanoscale*, 2011, **3**, 1663-1674.
- [4] P. Song, S. S. Li, L. L. He, J. J. Feng, L. Wu, S. X. Zhong and A. J. Wang, *RSC Adv.*, 2015, **5**, 87061-87068.

- [5] L. Chen, L. Kuai and B. Y. Geng, 2013, **15**, 2133-2136.
- [6] Y. J. Li, W. C. Ding, M. R. Li, H. B. Xia, D. Y. Wang and X. T. Tao, *J. Mater. Chem. A*, 2015, **3**, 368-376.
- [7] S. J. Guo, J. Li, S. J. Dong and E. K. Wang, , *J. Phys. Chem. C*, 2010, **114**, 15337-15342.
- [8] K. Mikkelsen, B. Cassidy, N. Hofstetter, L. Bergquist, A. Taylor and D. A. Rider, *Chem. Mater.*, 2014, **26**, 6928-6940.
- [9] J. Suntivich, Z. C. Xu, C. E. Carlton, J. Kim, B. H. Han, S. W. Lee, N. Bonnet, N. Marzari, L. F. Allard, H. A. Gasteiger, K. Hamad-Schifferli and Y. Shao-Horn, *J. Am. Chem. Soc.*, 2013, **135**, 7985-7991.
- [10] J. T. Zhang, H. Y. Ma, D. J. Zhang, P. P. Liu, F. Tian and Y. Ding, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3250-3255.
- [11] W. Hong, J. Wang and E. K. Wang, *Small*, 2014, **10**, 3262-3265.
- [12] Z. G. Guo, X. Zhang, H. Sun, X. P. Dai, Y. Yang, X. S. Li and T. T. Meng, *Electrochim Acta*, 2014, **134**, 411-417.
- [13] H. Atae-Esfahani, L. Wang, Y. Nemoto and Y. Yamauchi, *Chem. Mater.*, 2010, **22**, 6310-6318.