

Electronic Supplementary Information

Convenient Synthesis of Polymetallic Metal-Organic Gels for Efficient Methanol Electro-Oxidation

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S1: Additional characterization information

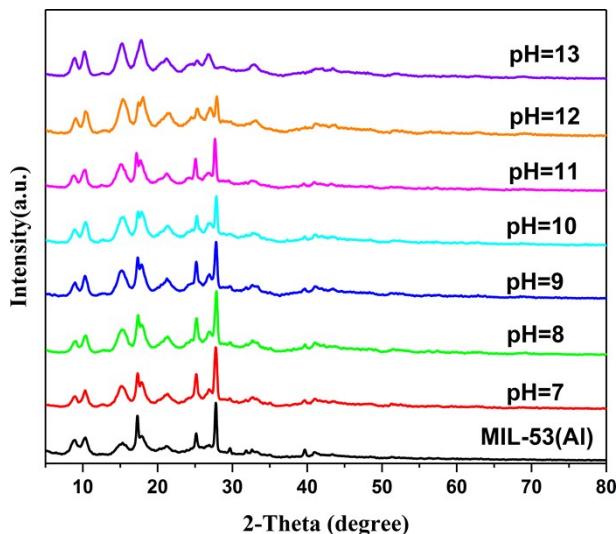


Fig. 1. MIL-53(Al)-MOG immersed in different pH environment for at least 24 h.

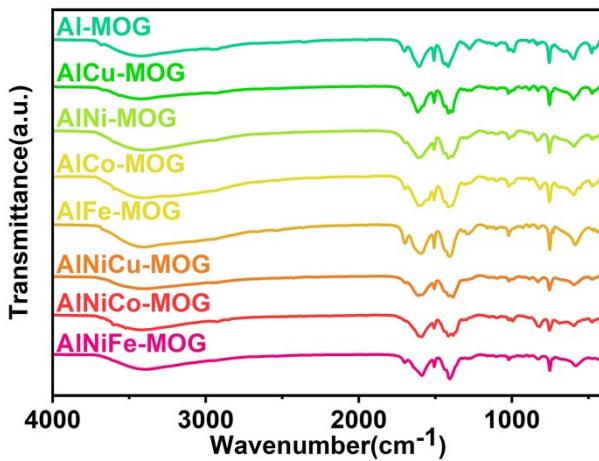


Fig. S2. FT-IR spectrums of the synthesized bimetallic and trimetallic MOGs.

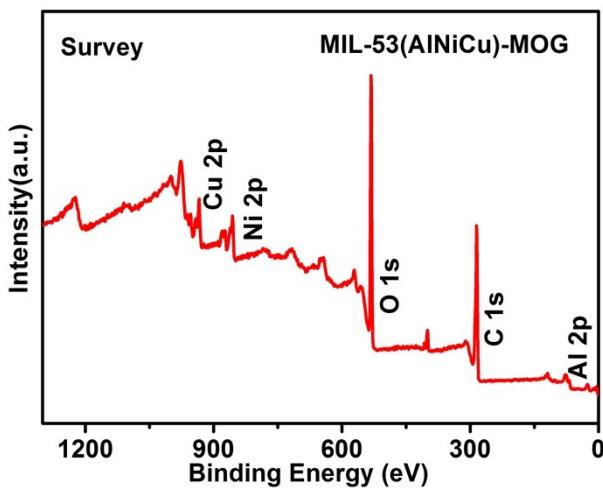


Fig. S3. The survey XPS spectra of the AlNiCu-MOG. Besides, the molar ratio of Al: Ni: Cu is close to 1:1:1, which was determined by inductively coupled plasma measurement.

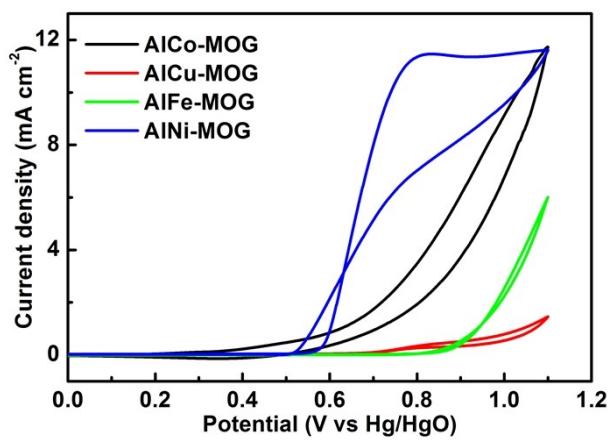


Fig. S4. CV curves for CH_3OH electro-oxidation of the bimetallic catalysts in the 0.1 M KOH with 1.0 M methanol.

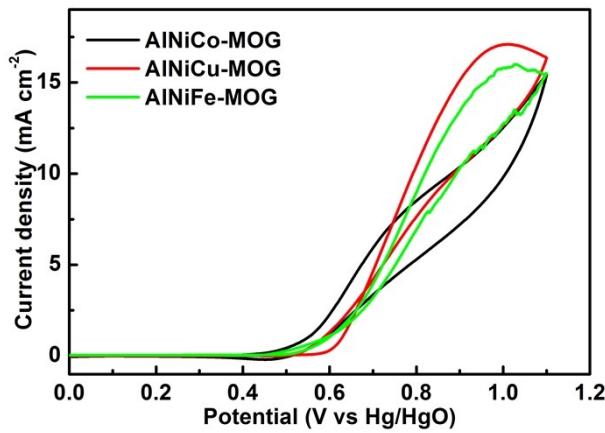


Fig. S5. CV curves for CH_3OH electro-oxidation of the trimetallic catalysts in the 0.1 M KOH with 1.0 M methanol.

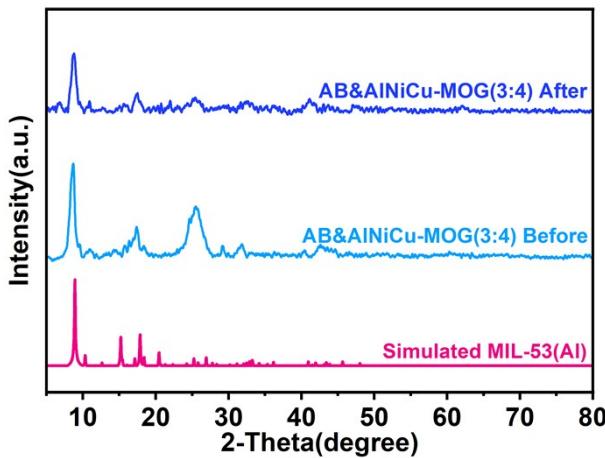


Fig. S6. The XRD patterns of the as-synthesized AB&AlNiCu-MOG (3:4) before and after MOR test.

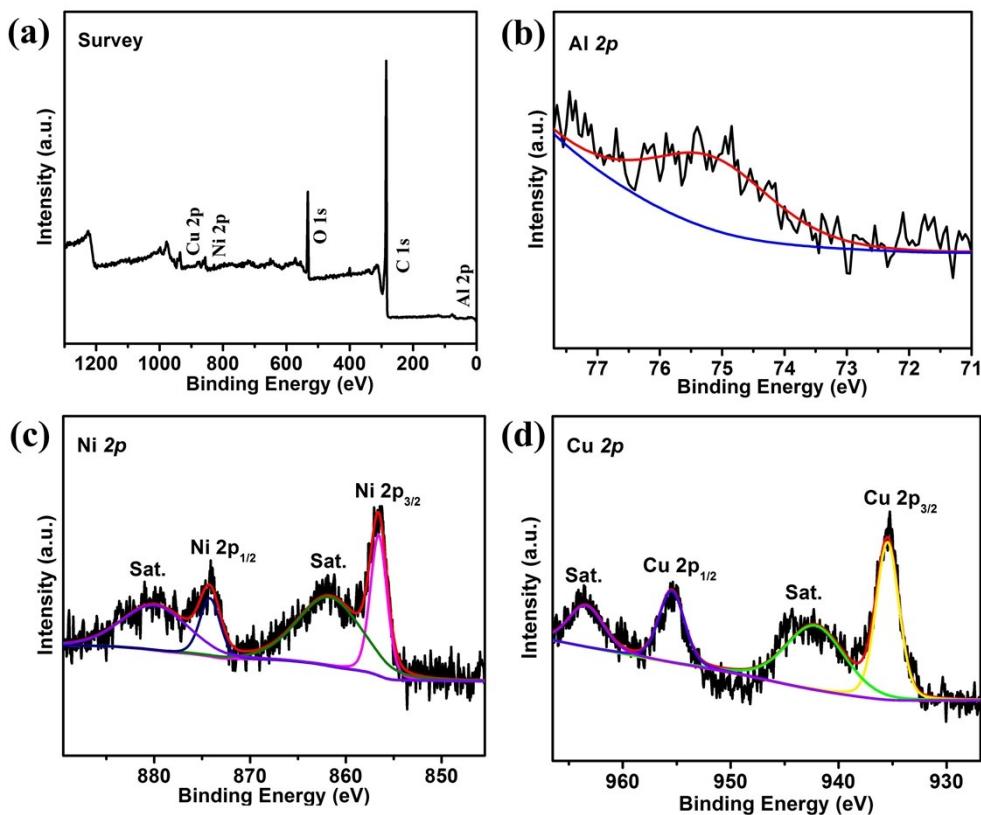


Fig. S7. XPS spectra (a) survey, (b) Al 2p, (c) Ni 2p and (d) Cu 2p of AB&AlNiCu-MOG (3:4) composite material.

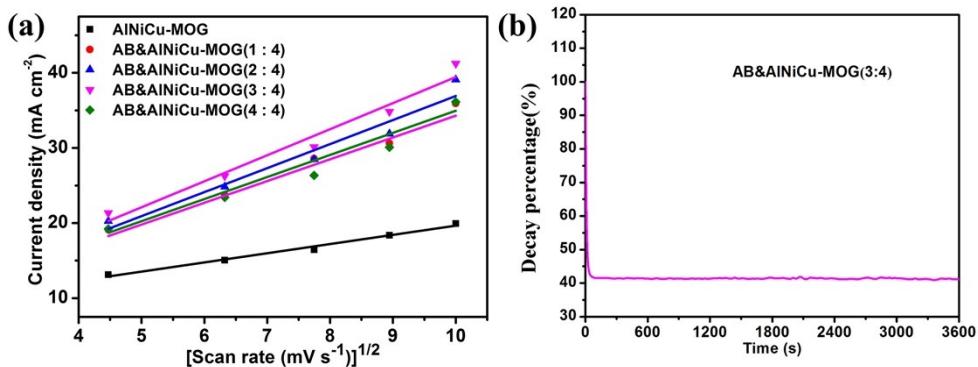


Fig. S8. (a) The linear relationship between current densities and square root of scan rates for AlNiCu-MOG and AB&AlNiCu-MOG composite materials. (b) Chronoamperometry plot of AB&AlNiCu-MOG (3:4) composite material in 0.1 M KOH with 1 M CH_3OH .

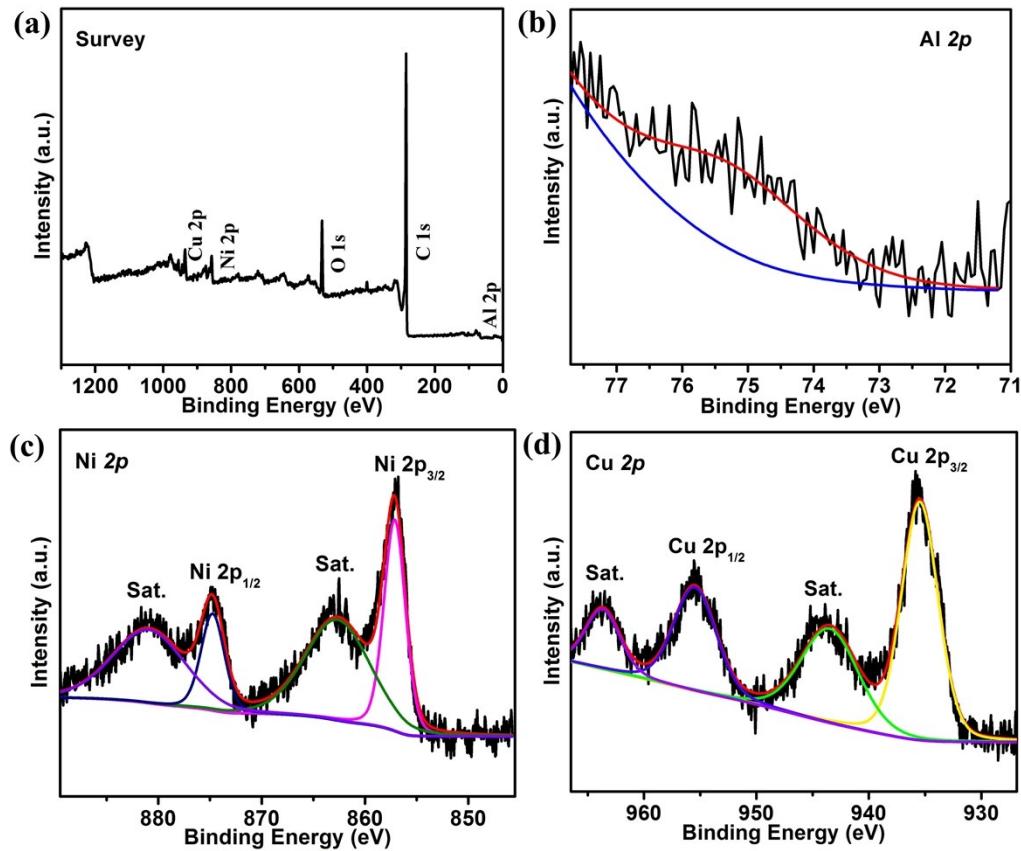


Fig. S9. XPS spectra (a) survey, (b) Al 2p, (c) Ni 2p and (d) Cu 2p of AB&AlNiCu-MOG (3:4) composite material after MOR test.

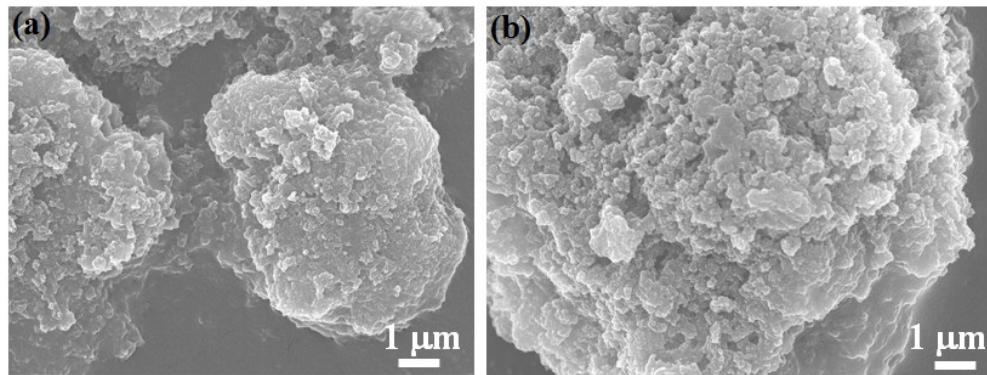


Fig. S10. SEM image of AB&AlNiCu-MOG (3:4) composite material (a) before and (b) after MOR stability measurements.

Table S1. Comparisons of MOR performance for various Ni-based electrocatalysts.

Electrode Materials	Scanning Rate (mV s ⁻¹)	Peak Current Density (mA cm ⁻²)		Electrolyte	Reference
		1	2)		
Ni-P/RGO	50	16.4		1.0M KOH + 0.5M CH ₃ OH	1
Mn Doped Ni(OH) ₂	50	16.7		1.0M KOH + 0.5M CH ₃ OH	2
NiPtAu-SR _{Au} HNCs	50	31.52		1.0M KOH + 1.0M CH ₃ OH	3
NiO NTs-400	50	24.3		1.0M KOH + 0.5M CH ₃ OH	4
PtZn intermetallic NPs	50	1.15		0.1M KOH + 0.5M CH ₃ OH	5
Pt ₁ Ni ₁ /C	50	4.90		1.0M KOH + 1.0M CH ₃ OH	6
NiO-Ni-P	50	28.56		1.0M KOH + 0.5M CH ₃ OH	7
NiO-SnO ₂ /SO ₄ ²⁻	100	12.2		1.0M NaOH + 1.0M CH ₃ OH	8
5 wt. % GO/Co-MOF-71	50	29.1		1.0M KOH + 3.0M CH ₃ OH	9
AlNi-MOG	50	11.46		0.1M KOH + 1.0M CH ₃ OH	
AlNiCu-MOG	50	17.1		0.1M KOH + 1.0M CH ₃ OH	
AB&AlNiCu-MOG(1 : 4)	50	29.33		0.1M KOH + 1.0M CH ₃ OH	this work
AB&AlNiCu-MOG(2 : 4)	50	32.31		0.1M KOH + 1.0M CH ₃ OH	
AB&AlNiCu-MOG(3 : 4)	50	33.24		0.1M KOH + 1.0M CH ₃ OH	
AB&AlNiCu-MOG(4 : 4)	50	29.41		0.1M KOH + 1.0M CH ₃ OH	

References

1. H. Zhang, C. Gu, M. Huang, X. Wang and J. Tu, Anchoring three-dimensional network structured Ni–P nanowires on reduced graphene oxide and their enhanced electrocatalytic activity towards methanol oxidation, *Electrochim. Commun.*, 2013, **35**, 108-111.
2. B. Dong, W. Li, X. Huang, Z. Ali, T. Zhang, Z. Yang and Y. Hou, Fabrication of hierarchical hollow Mn doped Ni(OH)₂ nanostructures with enhanced catalytic activity towards electrochemical oxidation of methanol, *Nano Energy*, 2019, **55**, 37-41.
3. C. Liu, Z. Chen, D. Rao, J. Zhang, Y. Liu, Y. Chen, Y. Deng and W. Hu, Behavior of gold-enhanced electrocatalytic performance of NiPtAu hollow nanocrystals for

alkaline methanol oxidation, *Sci. China Mater.*, 2020. DOI: <https://doi.org/10.1007/s40843-020-1460-y>.

4. T. Wang, H. Huang, X. Wu, H. Yao, F. Li, P. Chen, P. Jin, Z. Deng and Y. Chen, Self-template synthesis of defect-rich NiO nanotubes as efficient electrocatalysts for methanol oxidation reaction, *Nanoscale*, 2019, **11**, 19783-19790.
5. Z. Qi, C. Xiao, C. Liu, T. W. Goh, L. Zhou, R. Maligal-Ganesh, Y. Pei, X. Li, L. A. Curtiss and W. Huang, Sub-4 nm PtZn Intermetallic Nanoparticles for Enhanced Mass and Specific Activities in Catalytic Electrooxidation Reaction, *J. Am. Chem. Soc.*, 2017, **139**, 4762-4768.
6. S. Lu, H. Li, J. Sun and Z. Zhuang, Promoting the methanol oxidation catalytic activity by introducing surface nickel on platinum nanoparticles, *Nano Res.*, 2018, **11**, 2058-2068.
7. Y. Tong, C. Gu, J. Zhang, H. Tang, X. Wang and J. Tu, Thermal growth of NiO on interconnected Ni-P tube network for electrochemical oxidation of methanol in alkaline medium, *Int. J. Hydrogen Energ.*, 2016, **41**, 6342-6352.
8. Y. Gu, P. Gao, Z. Yu, Y. Hu, Z. Xu, C. Zhang, J. Li and Y. An, Honeycomb-like Mesoporous NiO-SnO₂/SO₄²⁻ Solid Superacid for the Efficient Reaction of Methanol Oxidation, *Int. J. Electrochem. Sci.*, 2020, **15**, 2481-2498.
9. R. Mehek, N. Iqbal, T. Noor, H. Nasir, Y. Mehmood and S. Ahmed, Novel Co-MOF/Graphene Oxide Electrocatalyst for Methanol Oxidation, *Electrochim. Acta*, 2017, **255**, 195-204.