

Supplementary Materials for

Boosting Ethanol Electrooxidation at RhBi Alloy and Bi₂O₃ Composite Surfaces in Alkaline Media

Yue Liu,^a Bing Lan,^a Yao-Yue Yang^{*a}

^aKey Laboratory of General Chemistry of State Ethnic Affairs Commission, School of Chemistry and Environment, Southwest Minzu University, Chengdu, 610041, Sichuan Province, China.

**Corresponding author, E-mail: yaoyueyoung@swun.edu.cn, ORCID ID: 0000-0002-4573-9437*

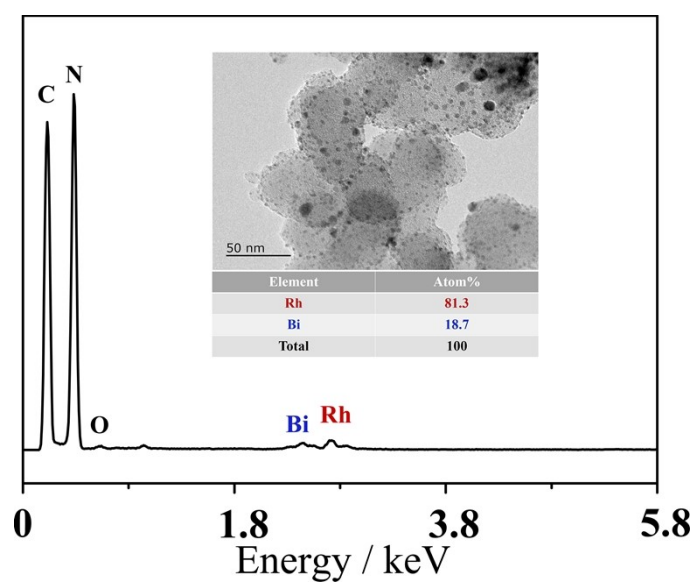


Figure S1. The typical energy-dispersive X-ray spectral (EDX) profile of RhBi-Bi₂O₃ catalysts which collected on randomly selected area during the corresponding transmission electron microscopy (TEM) characterization (the inset).

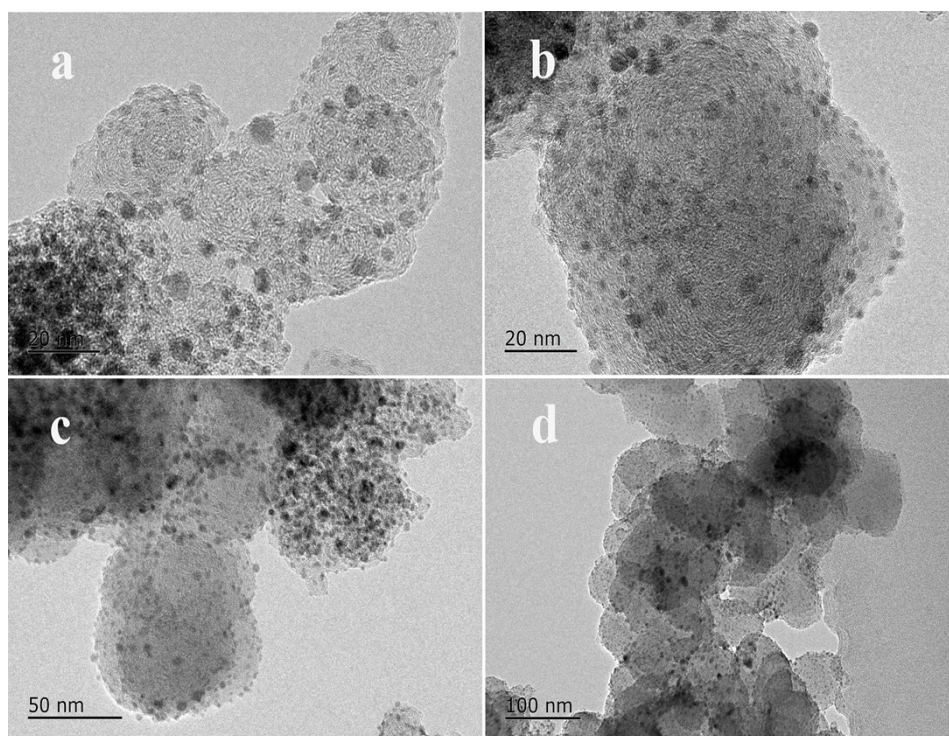


Figure S2. Typical HR-TEM images of the RhBi-Bi₂O₃ sample at different scales.

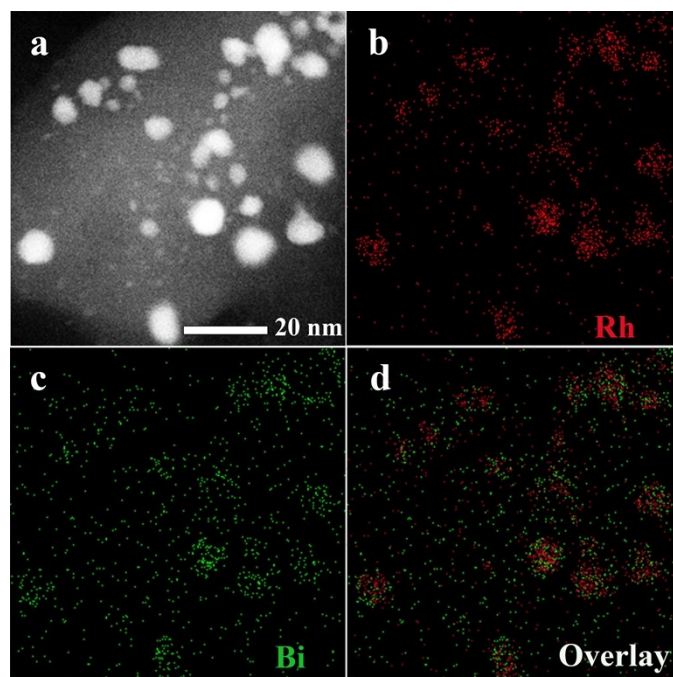


Figure S3. (a) High-angle annular dark field (HAADF) STEM image and (b-d) elemental mapping analysis of Rh and Bi elements for the RhBi-Bi₂O₃ sample.

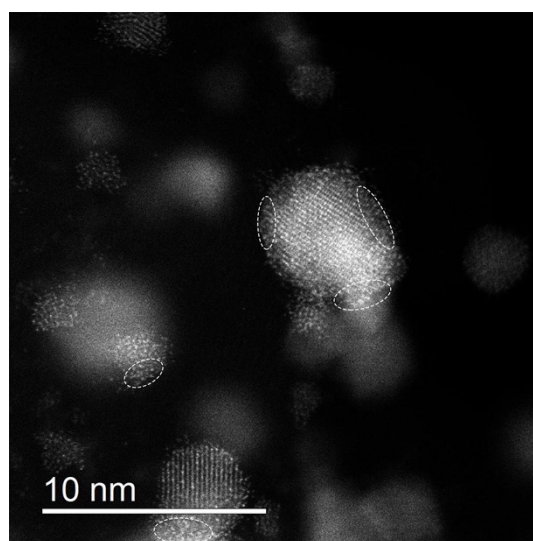


Figure S4. Typical High-resolution HAADF-STEM image of the as-prepared RhBi-Bi₂O₃ sample, and the flocculent structures are labeled by the white cycles.

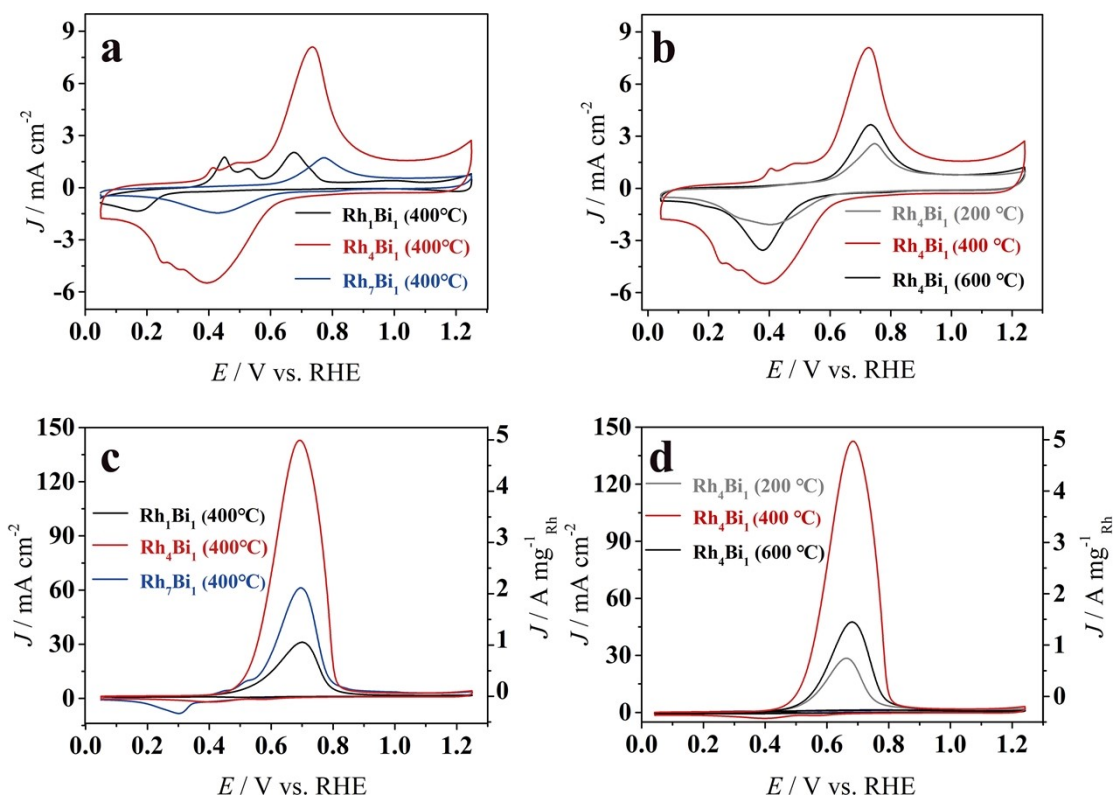


Figure S5. Cyclic voltammograms (CVs) collected on the Rh-based catalysts surfaces with different (a) Rh-to-Bi molar ratio and (b) annealing temperatures in 1 M NaOH and the corresponding CVs collected in 1 M NaOH+1 M C₂H₅OH solution (c-d) at the rate of 50 mV·s⁻¹.

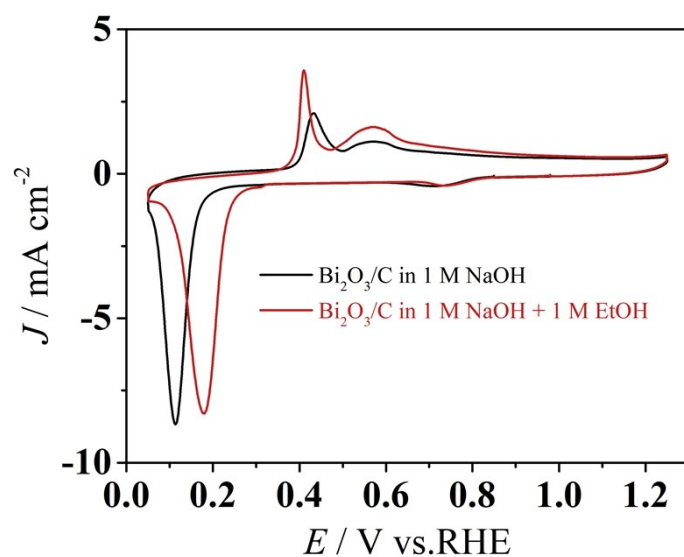


Figure S6. Cyclic voltammograms collected on the Bi₂O₃/C catalysts surfaces in 1 M NaOH and in 1 M NaOH + 1 M CH₃CH₂OH at the rate of 50 mV·s⁻¹.

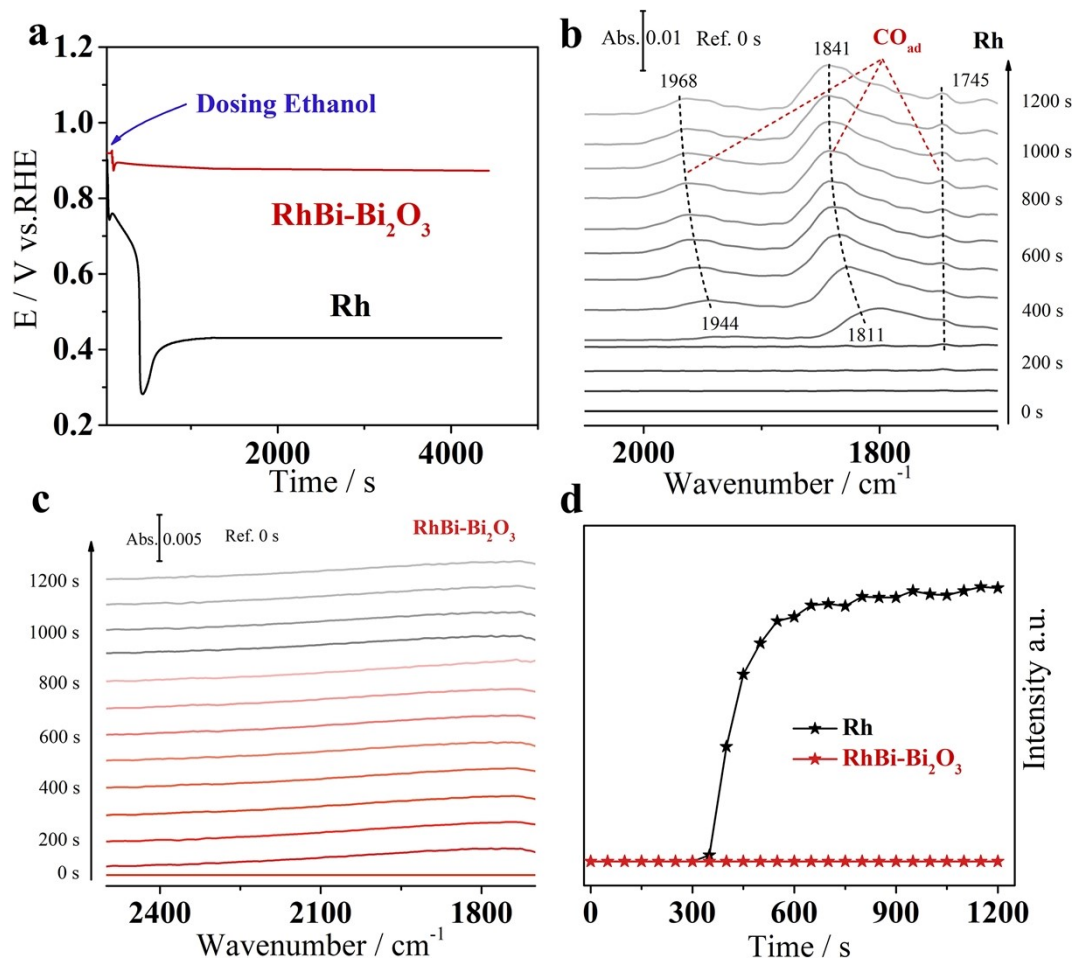


Figure S7. (a) OCP-t curves for the Rh and RhBi-Bi₂O₃ coated electrode in 0.1 M NaOH solution with the ethanol dosing at ca. 0 s. (b) and (c) respectively show the in situ electrochemical ATR-IR spectra collected on Rh and RhBi-Bi₂O₃ samples with ethanol injecting as described in (a), taken the single spectrum at 0 s as the reference spectrum. The corresponding potential-dependent band intensity variation of CO_{ad} species shown in (d). Spectral resolution is 8 cm⁻¹.

Table S1. A summary of the EOR activity and durability on Rh-based electrocatalysts surface in alkaline solution.

Sample	Electrolyte	Mass Activity (mA·mg _{Rh} ⁻¹)	stability	References
RhBi-Bi ₂ O ₃	1 M NaOH +1 M C ₂ H ₅ OH	5000	53.7 % activity retention after 10000 s	This work
Rh/C	1 M NaOH +1 M C ₂ H ₅ OH	60	0 % activity retention after 10000 s	This work
Rh-Bi(OH) ₃ /C	1 M NaOH +1 M C ₂ H ₅ OH	3500	34% activity retention after 7200 s	1
RhPb-PbO ₂ /C	1 M NaOH +1 M C ₂ H ₅ OH	2636	34% activity retention after 30000 s	2
SnO ₂ -Rh nanosheets	0.1 M KOH + 0.5 M C ₂ H ₅ OH	213.2	46% activity retention after 3600 s	3
Excavated RhNi Nanobranches	1 M NaOH +1 M C ₂ H ₅ OH	159.0	35% activity retention after 10000 s	4
Hollow porous Rh nanoballs	1 M NaOH +1 M C ₂ H ₅ OH	78.6	10% activity retention after 3600 s	5
Cyclic Penta- Twinned Rh nanobranches	1 M NaOH +1 M C ₂ H ₅ OH	185.3	75% activity retention after 1200 s	6
Porous PdRh nanobowls	1 M KOH +1 M C ₂ H ₅ OH	682.1	58% activity retention after 12000 s	7
Rh-on-Pd nanodendrites	1 M KOH +1 M C ₂ H ₅ OH	30.1-102.8	53.7%	8

Table S2. A summary of the *ECSA* and Peak Mass Activity on RhBi-Bi₂O₃,Pd/C-JM and Rh/C catalysts surface in alkaline solution.

Sample	<i>ECSA</i> (cm ⁻² ug ⁻¹)	Peak Mass Activity (mA mg ⁻¹ Rh)
RhBi-Bi ₂ O ₃	40.41	5000
Pd/C-JM	10.63	2000
Rh/C	6.06	60

References

1. B. Lan, Q. L. Wang, Z. X. Ma, Y. J. Wu, X. L. Jiang, W. S. Jia, C. X. Zhou and Y. Y. Yang, *Appl. Catal. B-Environ.*, 2022, **300**, 120728-120734.
2. B. Lan, M. Huang, R. L. Wei, C. N. Wang, Q. L. Wang and Y. Y. Yang, *Small*, 2020, **16**, 2004380-2004385.
3. S. X. Bai, Y. Xu, K. L. Cao and X. Q. Huang, *Adv. Mater.*, 2021, **33**, 2005767-2005777.
4. H. Q. Li, J. Y. Ye, X. M. Li, J. W. Zhang, Y. F. Zhu, Z. Y. Zhou, Y. K. Xue, Y. Q. Jiang, Z. X. Xie and L. S. Zheng, *J. Mater. Chem. A*, 2019, **7**, 26266-26271.
5. J. W. Zhang, Y. T. Jiang, S. L. Shi, H. Q. Li, J. Y. Chen, Q. Kuang, Z. X. Xie and L. S. Zheng, *Chem. Commun.*, 2019, **55**, 4989-4992.
6. J. W. Zhang, J. Y. Ye, Q. Y. Fan, Y. T. Jiang, Y. F. Zhu, H. Q. Li, Z. M. Cao, Q. Kuang, J. Cheng, J. Zheng and Z. X. Xie, *J. Am. Chem. Soc.*, 2018, **140**, 11232-11240.
7. Z. J. Li, Y. F. Chen, G. T. Fu, Y. Chen, D. M. Sun, J. M. Lee and Y. W. Tang, *Nanoscale*, 2019, **11**, 2974-2980.
8. S. Y. Shen and T. S. Zhao, *J. Mater. Chem. A*, 2013, **1**, 906-912.