

Supplementary Material

Noble-metal-free $\text{Ni}_{10}\text{MoCo}_x/\text{Mo-Ni-O}$ as an active and durable catalyst for hydrogen generation from hydrazine monohydrate

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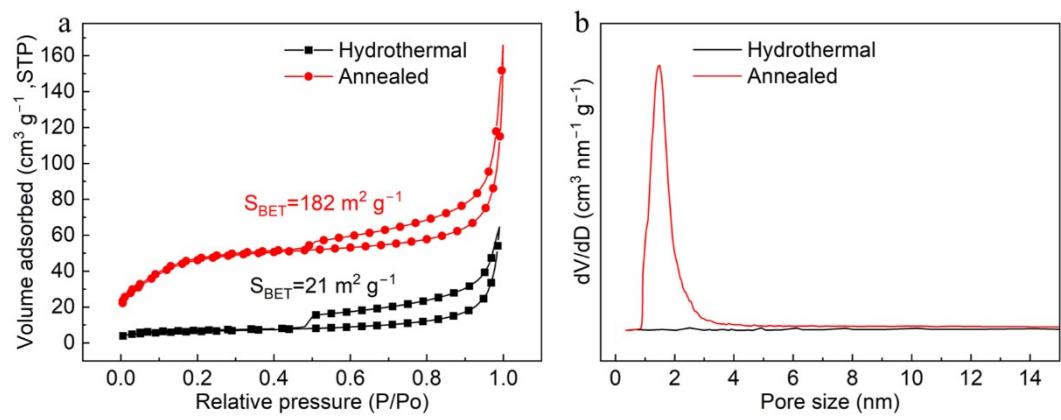


Figure S1. (a) N₂ adsorption-desorption isotherms and (b) pore size distributions of the hydrothermal and annealed samples.

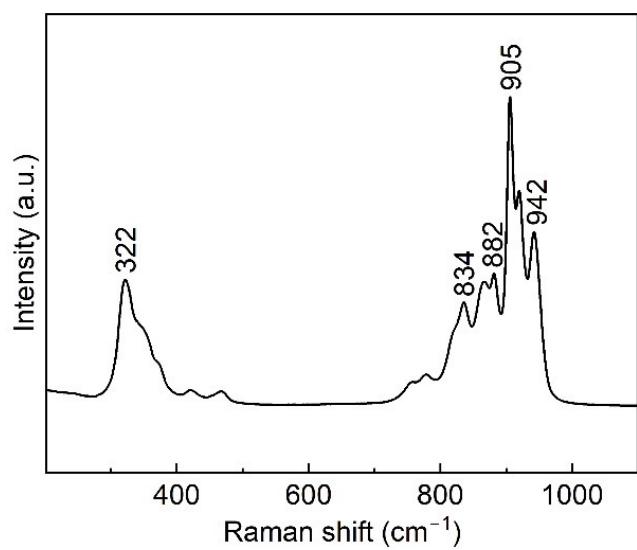


Figure S2. Raman spectrum of the hydrothermal sample.

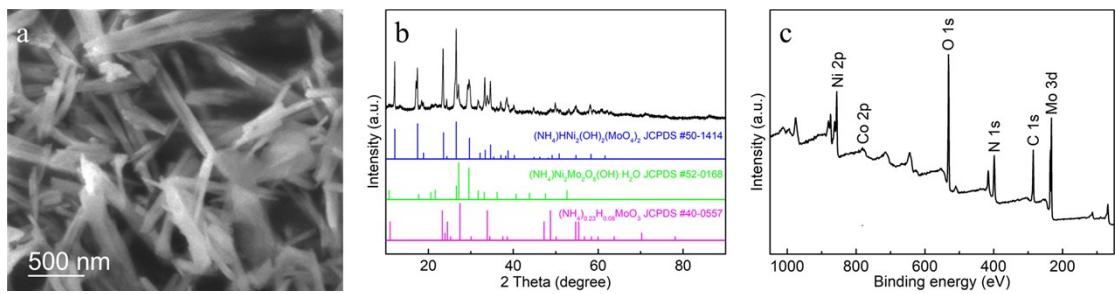


Figure S3. (a) FE-SEM image, (b) XRD pattern and (c) XPS spectrum of the SEA sample.

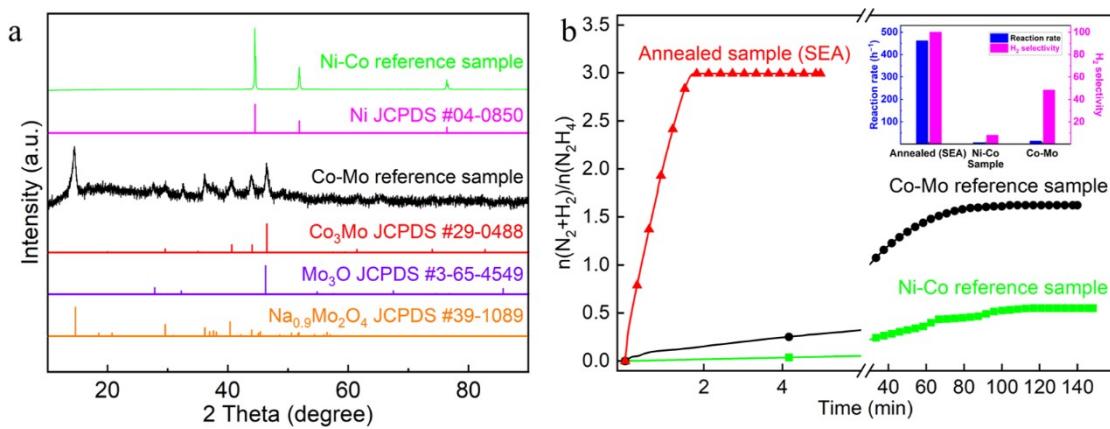


Figure S4. (a) XRD patterns of Ni-Co and Co-Mo reference samples. (b) Kinetic curves of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ decomposition over the annealed sample (SEA) and Ni-Co, Co-Mo reference samples. The inset shows the reaction rate and H_2 selectivity of the samples. The catalytic decomposition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was carried out in a 2 mL solution containing 0.5 M $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 2.0 M NaOH at 70 °C, with metal/ N_2H_4 ratio of 1:10.

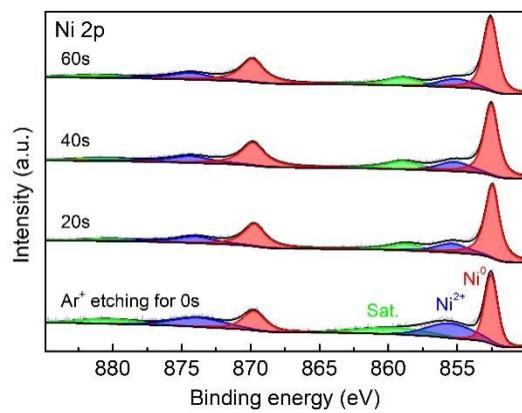


Figure S5. Ni 2p spectra of the annealed sample (SEA) as a function of etching time.

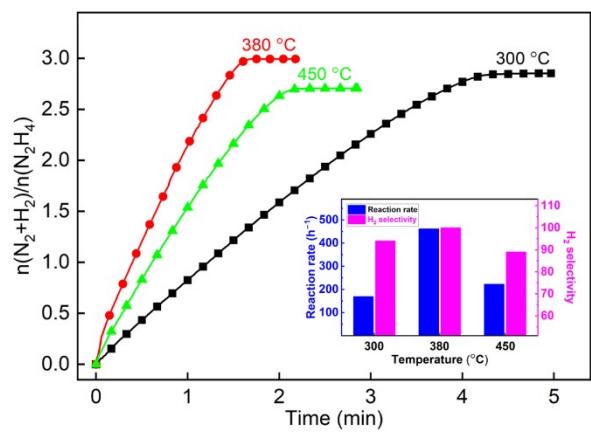


Figure S6. Kinetic curves of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ decomposition over the $\text{Ni}_{10}\text{MoCo}_x/\text{Mo-Ni-O}$ catalyst annealed at different temperatures. The inset displays the reaction rate and H_2 selectivity as a function of annealing temperature. The catalytic decomposition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was carried out in a 2 mL solution containing 0.5 M $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 2.0 M NaOH, with metal/ N_2H_4 ratio of 1:10.

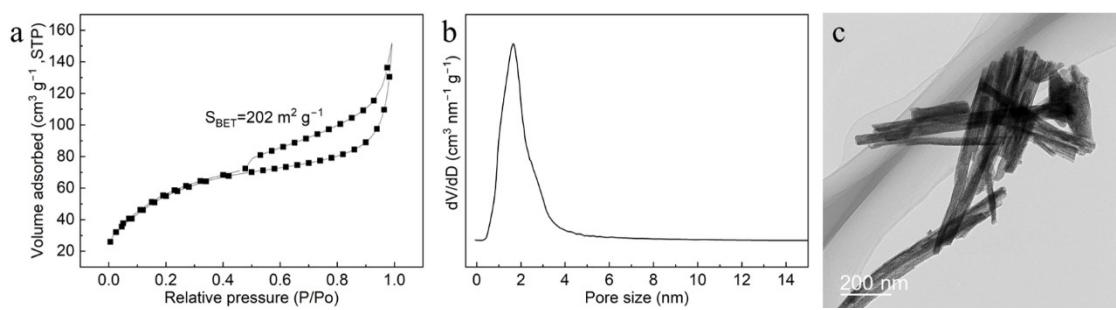


Figure S7. (a) N_2 adsorption-desorption isotherms, (b) pore size distributions and (c) TEM image of the $\text{Ni}_{10}\text{Mo}/\text{Mo}-\text{Ni}-\text{O}$ catalyst.

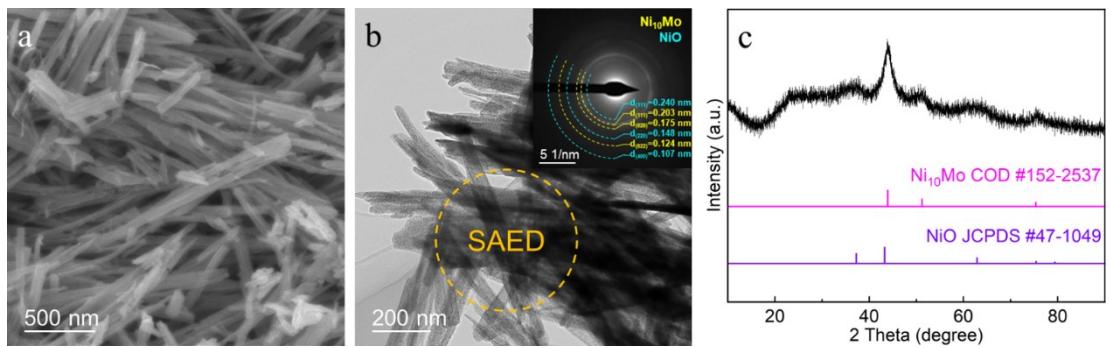


Figure S8. (a) FE-SEM image, (b) TEM image and the corresponding SAED pattern (inset) and (c) XRD pattern of the post-used Ni₁₀MoCo_x/Mo-Ni-O (SEA) sample.

Table S1. A comparison of catalytic properties of $\text{Ni}_{10}\text{MoCo}_x/\text{Mo-Ni-O}$ and relevant catalysts for H_2 generation from $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

Catalyst	Temperature (°C)	Reaction rate (h^{-1})	E_a (kJ mol $^{-1}$)	Reference
NiMoB-La(OH) ₃	50	13.3	/	1
$\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$	50	33	/	2
Ni/CeO ₂	50	34	56.2	3
$\text{Ni}_{10}\text{Mo}/\text{Ni-Mo-O}$	50	54.5	55.8	4
Ni@TNTs	60	96	53.2	5
Cu@Fe ₅ Ni ₅	70	11.9	79.2	6
FeNi/Cu	70	17.6	44	7
$\text{Ni}_{0.9}\text{Fe}_{0.1}\text{-Cr}_2\text{O}_3$	70	82.2	86.3	8
CuNi/La ₂ O ₂ CO ₃ /rGO	70	114.3	65.5	9
$\text{Ni}_3\text{Fe-(CeO}_x\text{)}_{0.15}/\text{rGO}$	70	126.2	34.3	10
$\text{Ni}_{10}\text{MoCo}_x/\text{Mo-Ni-O}$	50	122	51.5	This work
	70	461		

References

1. J. Zhang, Q. Kang, Z. Yang, H. Dai, D. Zhuang, P. Wang, *J. Mater. Chem. A*, 2013, **1**, 11623–11628.
2. Q. Shi, D. X. Zhang, H. Yin, Y. P. Qiu, L. L. Zhou, C. Chen, H. Wu, P. Wang, *ACS Sustainable Chem. Eng.*, 2020, **8**, 5595–5603.
3. W. Kang, A. Varma, *Appl. Catal., B*, 2018, **220**, 409–416.
4. Y. P. Qiu, G. X. Cao, H. Wen, Q. Shi, H. Dai, P. Wang, *Int. J. Hydrogen Energy*, 2019, **44**, 15110–15117.
5. H. Wang, L. Wu, A. Jia, X. Li, Z. Shi, M. Duan, Y. Wang, *Chem. Eng. J.*, 2018, **332**, 637–646.
6. J. Wang, Y. Li, Y. Zhang, *Adv. Funct. Mater.*, 2014, **24**, 7073–7077.
7. K. V. Manukyan, A. Cross, S. Rouvimov, J. Miller, A. S. Mukasyan, E. E. Wolf, *Appl. Catal., A*, 2014, **476**, 47–53.
8. J. Chen, H. Zou, Q. Yao, M. Luo, X. Li, Z. H. Lu, *Appl. Surf. Sci.*, 2020, **501**, 144247.
9. X. Hong, Q. Yao, J. Long, X. Li, X. Chen, Z. H. Lu, *Ind. Eng. Chem. Res.*, 2021, **60**, 16224–16232.
10. Y. Men, X. Du, G. Cheng, W. Luo, *Int. J. Hydrogen Energy*, 2017, **42**, 27165–27173.