Electronic Supporting Information

Enhanced Electrochemical Nitrate Reduction to Ammonia with Nanostructured Mo₂C on Carbon Nanotube-Reduced Graphene Oxide Hybrid Support

So Eun Jang,[a] Jae Young Kim[*b] and Duck Hyun Youn[*a]

[a]Department of Chemical Engineering, Department of Integrative Engineering for Hydrogen Safety, Kangwon Nation University, Cheucheon 24341, South Korea.
[b]Korea Research Institute of Chemical Technology, Daejeon 34114, South Korea.

*Corresponding authors

E-mail address: youndh@kangwon.ac.kr, jaeykim@krict.re.kr

Determination of ion concentration

Determination of NO_3^- :

Firstly, a certain volume of electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Then, 0.1 mL of 1 M HCl was added into the aforementioned solution. After 5 minutes, the absorbance was measured by UV-Vis spectrophotometer at a wavelength of 220 nm. The concentration-absorbance curve was calibrated using a series of standard sodium nitrate solutions.

Determination of NO_2^- :

The concentration of nitrite was analyzed using the typical Griess method. A mixture of p-aminobenzenesulfonamide (4.0 g), N-(1-Naphthyl) ethylenediamine dihydrochloride (0.2 g), ultrapure water (50 mL) and phosphoric acid (10 mL) was used as the color reagent. A certain volume of electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Then, 0.1 mL color reagent was added into the aforementioned 5 mL sample and mixed uniformly. After 20 minutes, the absorbance at 540 nm was measured by UV-Vis spectrophotometer. The concentration-absorbance curve was calibrated using a series of standard sodium nitrite solutions.

Determination of NH_3 :

The concentration of ammonia was determined using Nessler's reagent method. First, a certain volume of electrolyte was taken out from the electrolytic cell and diluted to 5 ml to detection range. Then, 0.1 mL potassium sodium tartrate solution and 0.1 mL Nessler's reagent were added into the above 5 mL sample and mixed uniformly. After 20 minutes, the absorbance at 420 nm was measured by UV-Vis spectrophotometer. The concentration-absorbance curve was calibrated using a series of standard ammonium chloride solutions.

¹⁵N Isotope Labeling Experiments :

Isotope labeling experiments were performed using $Na^{15}NO_3{}^{-}$-^{15}N as a nitrogen source to confirm the origin of generated ammonia. After chronoamperometry tests, 20 mL of the electrolyte was taken out and the pH value was adjusted to be weak acid with HCl. After that, the adjusted electrolyte was concentrated to about 3 mL via rotary evaporator. 950 μL of the condensed solution was mixed with 50 μL of DMSO-d_6. The mixed solution was analyzed using ^1H NMR (600 MHz). $^{14}NH_4Cl$ and $^{15}NH_4Cl$ solutions were measured to obtain the standard triplet and doublet peaks, following the same procedure.

Calculation of the yield and Faradaic efficiency

The ammonia yield rate (mg h^{-1} cm^{-2}) was calculated by the Eq. (1) :

$$\text{Yield} = \frac{C_{NH3} \times V}{m_{NH3} \times t \times A} \tag{1}$$

The Faradaic efficiency (FE$_{NH3}$) was calculated by the Eq. (2) :

$$\text{FE}_{NH3} = \frac{n \times F \times C_{NH3} \times V}{m_{NH3} \times Q} \times 100\,\% \tag{2}$$

where C_{NH3} is the measured ammonia concentration (mg L^{-1}), V is the volume of electrolyte (30 mL), m_{NH3} is the molar mass of ammonia, t is the electrolysis time (1 h), A is the area of the working electrode (1 x 1 cm^2), n is the number of electrons transferred, which is 8 for

ammonia and 2 for nitrite. F is faradaic constant (96485 C mol^{-1}), Q is the total charge passing the electrode.

Adsorption capacity measurements

To determine the adsorption capacities of the synthesized catalysts, a certain amount of each catalyst was added to 30 mL of nitrate solutions with an initial concentration of 0.1 M. The mixtures were stirred for 2 hours. After stirring, the solutions were separated by filtration using the 0.45 μm microporous membrane filter. Specifically, the solution was diluted before absorbance measurements. The adsorption capacity was calculated by the Eq. (3) :

$$q_e = \frac{(C_0 - C_e) \times V}{m_{cat.}} \tag{3}$$

where q_e is the adsorption capacity (g g$_{cat.}$$^{-1}$), C_0 is the initial concentration of nitrate (g mL^{-1}), C_e is the measured concentration of nitrate after the adsorption (g mL^{-1}), V is the volume of the electrolyte (30 mL), $m_{cat.}$ is the mass of the catalyst (g).
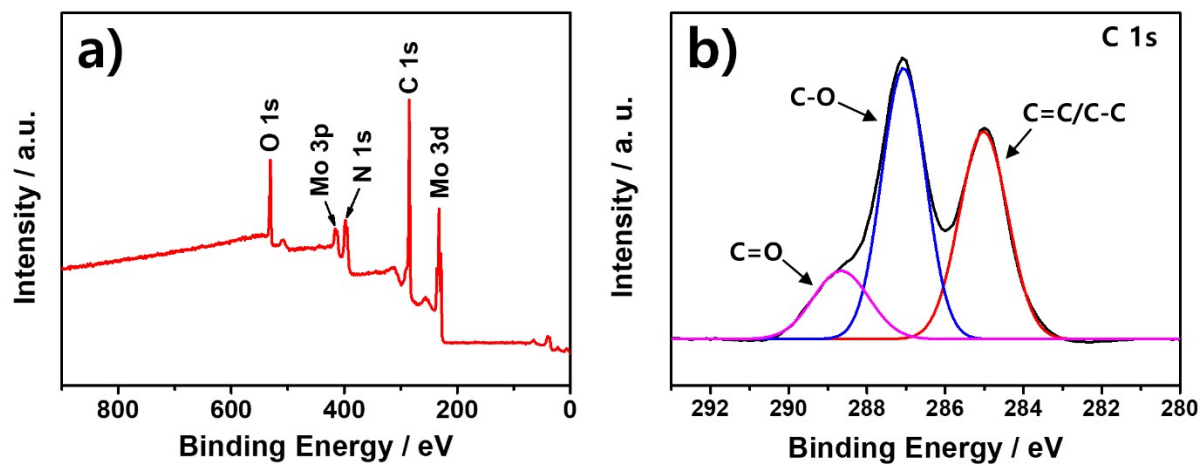
Fig. S1 a) XPS survey scan of Mo₂C/CNT-RGO. b) XPS spectra of GO for C 1s
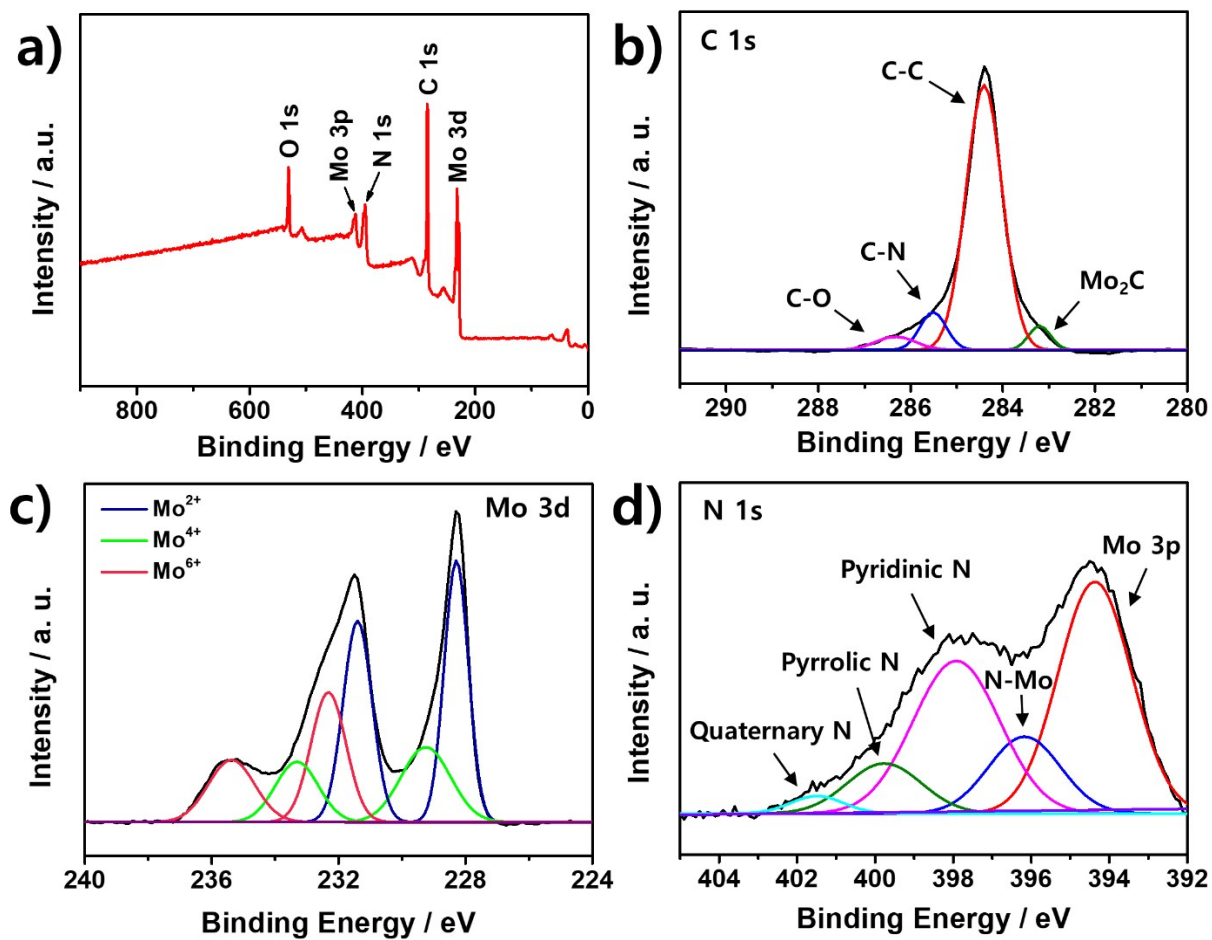
Fig. S2 XPS spectra of Mo$_2$C/CNT for a) survey scan, b) C 1s, c) Mo 3d, and d) N 1s.
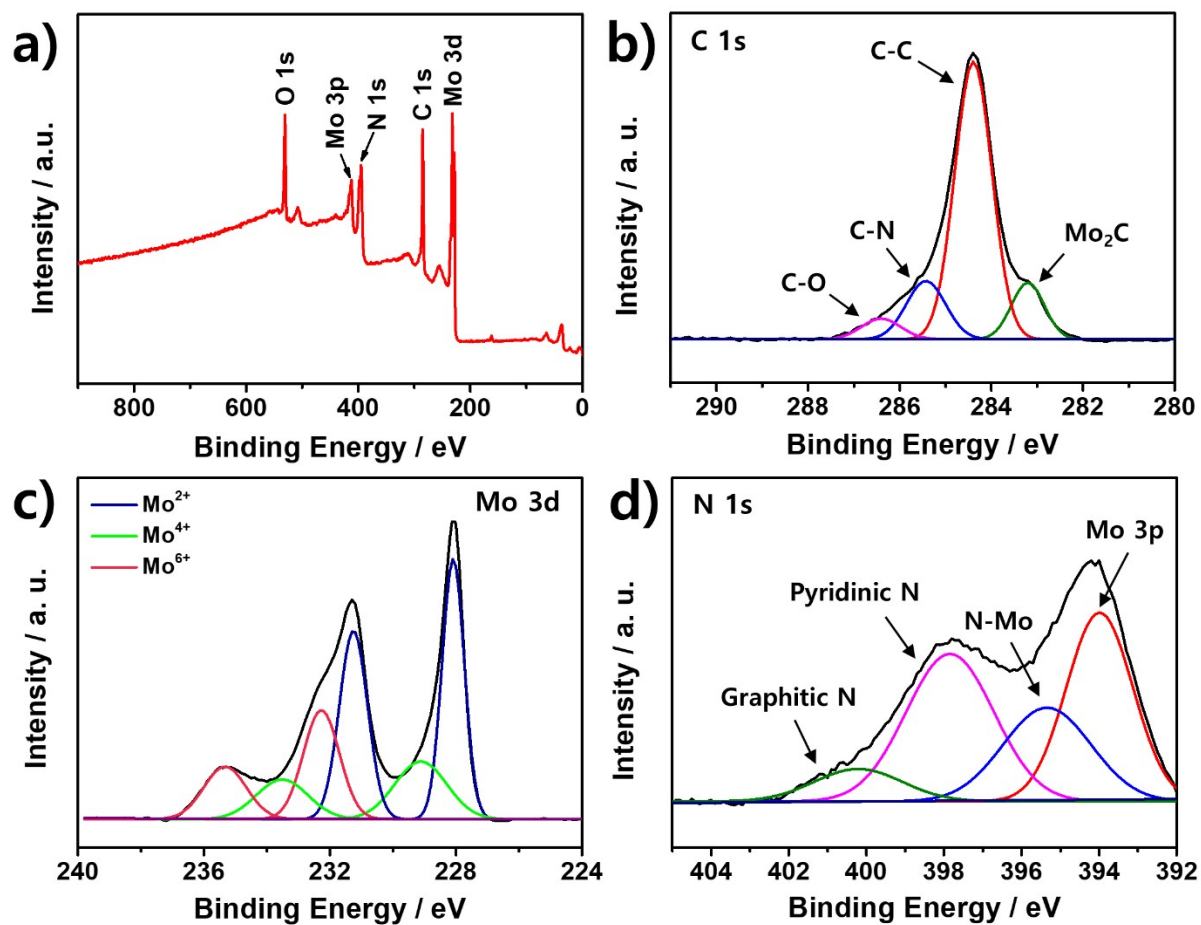
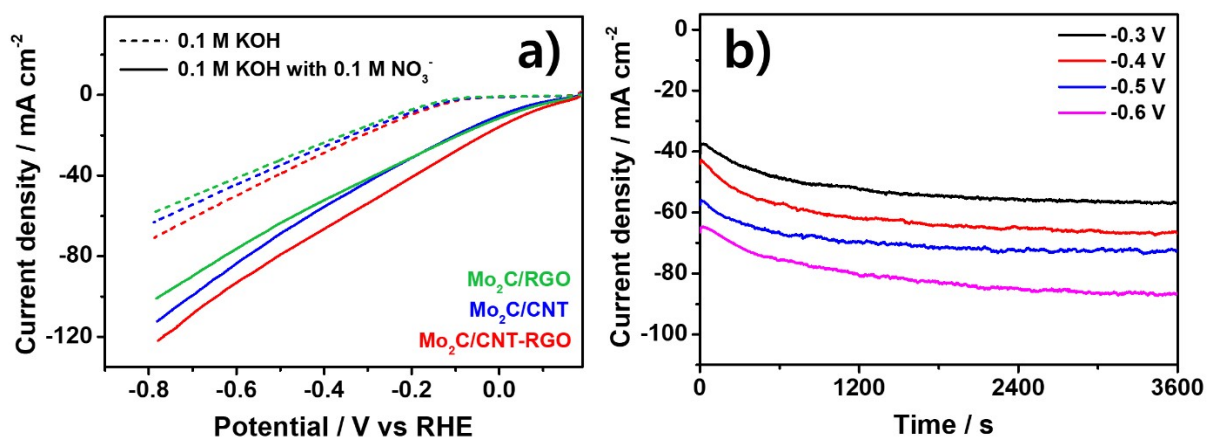**Fig. S3** XPS spectra of Mo$_2$C/RGO for a) survey scan, b) C 1s, c) Mo 3d, and d) N 1s.

Fig. S4 a) LSV curves for as-prepared catalysts in 0.1 M KOH with and without 0.1 M NaNO$_3$. b) Chronoamperometry measurements of the Mo$_2$C/CNT-RGO electrode at different given potentials in NO$_3^-$RR.
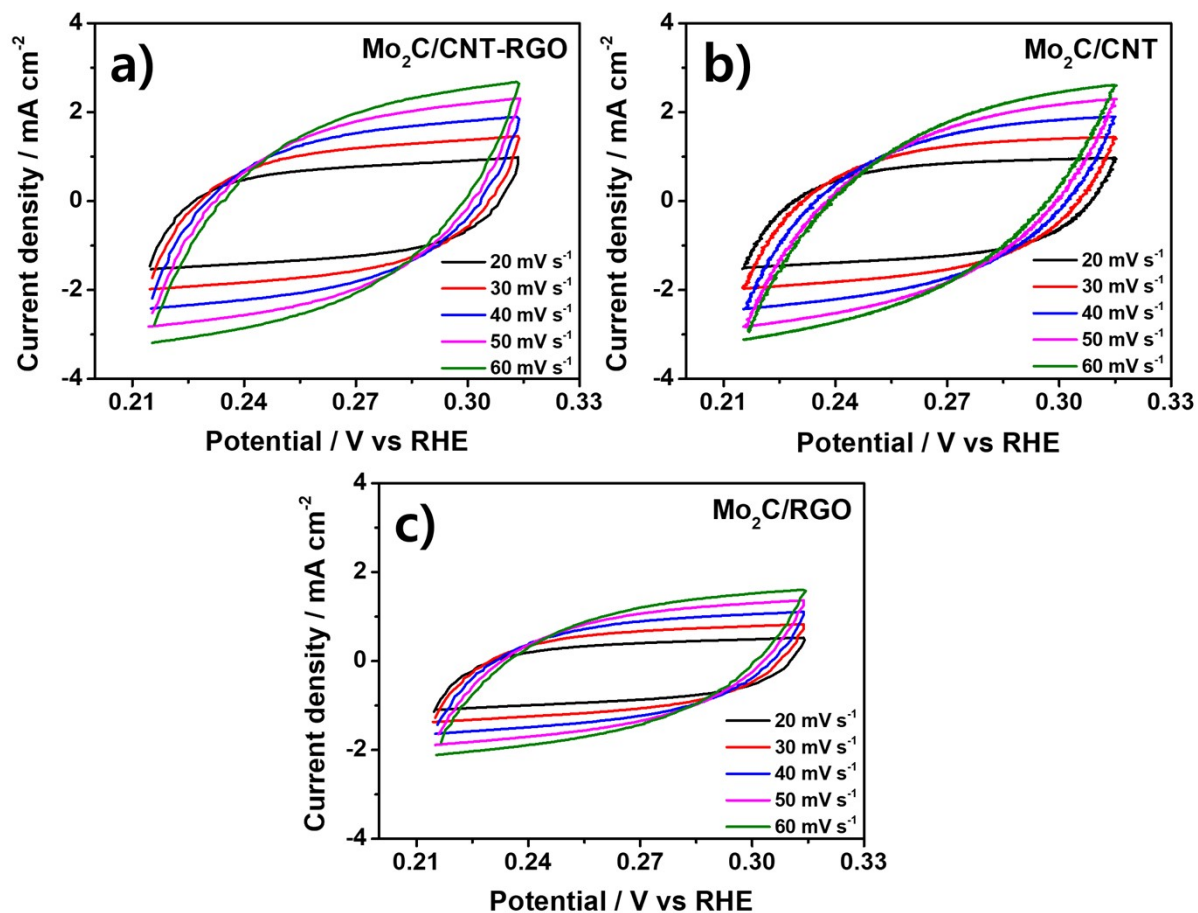
Fig. S5 Cyclic voltammograms of a) Mo$_2$C/CNT-RGO, b) Mo$_2$C/CNT, and c) Mo$_2$C/RGO with various scan rates (20 to 60 mV s^{-1}) at the potential range of 0.21 - 0.31 V vs RHE.
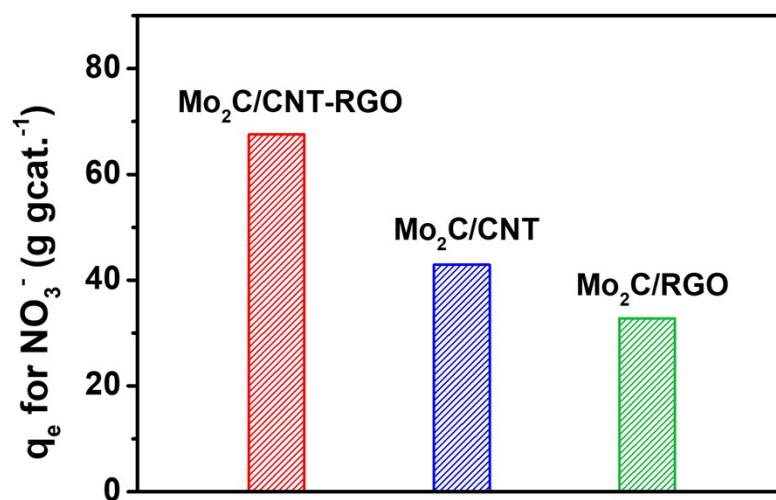
Fig. S6 Adsorption capacities of Mo_2C/CNT-RGO, Mo_2C/CNT, and Mo_2C/RGO for NO_3^-.
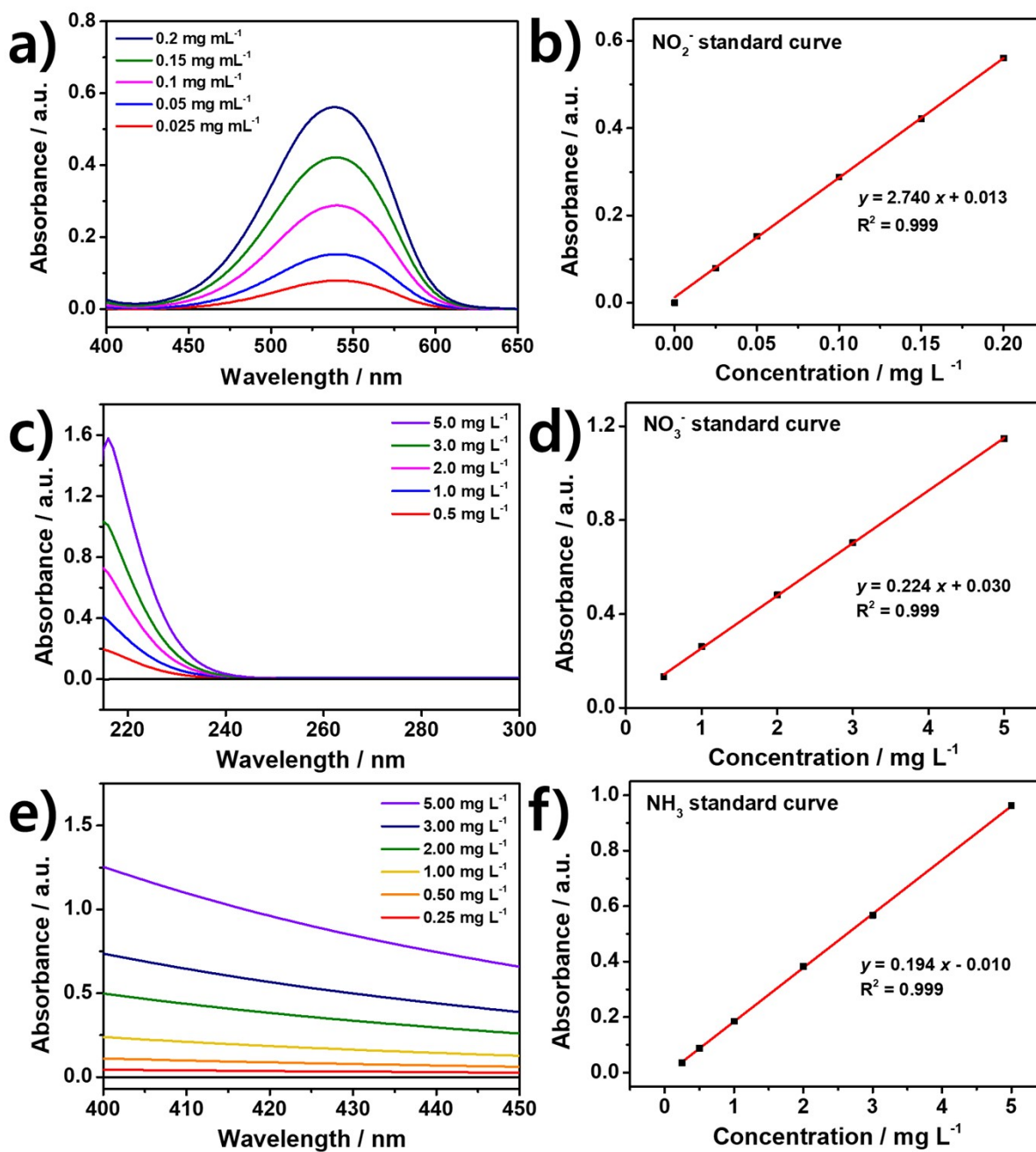
Fig. S7 a) UV-vis adsorption spectra and b) calibration curves for NO_2^-. c) UV-vis adsorption spectra and d) calibration curves for NO_3^-. e) UV-vis adsorption spectra and f) calibration curves for NH_3.
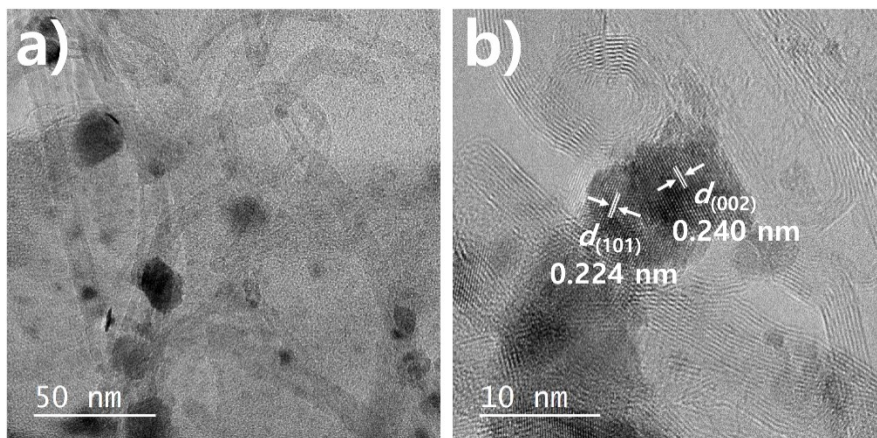
Fig. S8 TEM and HRTEM images of a, b) Mo₂C/CNT-RGO after consecutive cycling test.

Table S1. The comparison of NH$_3$ yield and FE with other Mo-based catalysts for NO$_3^-$RR.

Catalysts	Electrolyte	FE	NH$_3$ yield	Ref.
Mo$_2$C NS	1 M NaOH + 0.1 M NO$_3^-$	81.4 % (@ -0.3 V)	18.87 mg h^{-1} mg$_{cat.}^{-1}$ (@ -0.3 V)	[1]
Mo$_2$C/RGO	0.5 M Na$_2$SO$_4$ + 0.1 M NO$_3^-$	85.2 % (@ -0.6 V)	4.8 mg h^{-1} cm^{-2} (@ -0.6 V)	[2]
Mo/TiO$_2$	0.05 M Na$_2$SO$_4$ + 0.1 M KNO$_3$	88.0 % (@ -1.4 V)	3.0 mg h^{-1} cm^{-2} (@ -1.4 V)	[3]
NiMoO$_4$	0.5 M Na$_2$SO$_4$ + 0.05 M NaNO$_3$	96.13 % (@ -0.4 V)	0.22 mg h^{-1} cm^{-2} (@ -0.4 V)	[4]
Fe-MoS$_2$	0.1 M Na$_2$SO$_4$ + 0.1 M NaNO$_3$	98 % (@ -0.5 V)	0.51 mg h^{-1} cm^{-2} (@ -0.5 V)	[5]
FeMo-N-C	0.05 M PBS + 0.16 M NO$_3^-$	94.7 % (@ -0.45 V)	0.30 mg h^{-1} cm^{-2} (@ -0.45 V)	[6]
Bi$_2$S$_3$/MoS$_2$/CC	0.1 M Na$_2$SO$_4$ + 0.1 M NaNO$_3$	88.4 % (@ -0.8 V)	2.56 mg h^{-1} cm^{-2} (@ -0.8 V)	[7]
1T-MoS$_2$	0.5 M K$_2$SO$_4$ + 0.1 M KNO$_3$	88.1 % (@ -0.5 V)	0.65 mg h^{-1} cm^{-2} (@ -0.5 V)	[8]
FeMoN@C NO	1 M KOH + 0.1 M NaNO$_3$	98.2 % (@ -0.3 V)	7.39 mg h^{-1} cm^{-2} (@ -0.3 V)	[9]
Mo$_2$C/CNT-RGO	**0.1 M KOH + 0.1 M NaNO$_3$**	**95.9 % (@ -0.3 V)**	**5.23 mg h^{-1} cm^{-2} (@ -0.6 V)**	**This Work**
Mo$_2$C/CNT	**0.1 M KOH + 0.1 M NaNO$_3$**	**85.3 % (@ -0.3 V)**	**4.55 mg h^{-1} cm^{-2} (@ -0.6 V)**	**This Work**
Mo$_2$C/RGO	**0.1 M KOH + 0.1 M NaNO$_3$**	**84.4 % (@ -0.3 V)**	**4.52 mg h^{-1} cm^{-2} (@ -0.6 V)**	**This Work**

References

1   D. Zhu, G. Li, X. Yan, C. Geng and L. Gao, *Sci. Total Environ.,* 2023, **878**, 163145.

2   X. Li, S. Wang, G. Wang, P. Shen, D. Ma and K. Chu, *Dalton Trans.,* 2022, **51,** 17547-17552.

3   H. Chen, W. Hu, T. Ma, Y. Pu, S. Wang, Y. Wang and S. Yuan, *Molecules*, 2024, **29**, 2782.

4   D. Li, J. Chen, S. Sun, C. Xu, Y. Sun, H. Mou, D. Wang and C. Song, *ACS Appl. Nano Mater.,* 2024, **7**, 13338-13346.

5   J. Li, Y. Zhang, C. Liu, L. Zheng, E. Petit, K. Qi, Y. Zhang, H. Wu, W. Wang, A. Tiberj, X. Wang, M. Chhowalla, L. Lajaunie, R. Yu and D. Voiry, *Adv. Funct. Mater.*, 2022, **32**, 2108316.

6   E. Murphy, Y. Liu, I. Matanovic, S. Guo, P. Tieu, Y. Huang, A. Ly, S. Das, I. Zenyuk, X. Pan, E. Spoerke and P. Atanassov, *ACS Catal.*, 2022, **12**, 6651-6662.

7   X. Liu, X. Xu, F. Li, J. Xu, H. Ma, X. Sun, D. Wu, C. Zhang, X. Ren and Q. Wei, *ACS Appl. Mater. Interfaces*, 2022, **14**, 38835-38843.

8   Y. Wang, Y. Xu, C. Cheng, B. Zhang, B. Zhang and Y. Yu, *Angew. Chem.*, 2024, **136**, e202315109.

9   J. Yan, P. Liu, J. Li, H. Huang, S. Tong and W. Song, *Chem. Eng. J.*, 2024, **498**, 155108.