

Electronic Supporting Information (ESI)

**Nickel Nanoparticles Wrapped in N-doped Carbon Nanostructures for
Efficient Electrochemical Reduction of NO to NH₃**

Muthusamy Tamilselvan^a, Sridhar Sethuram Markandaraj^a and Sangaraju Shanmugam^{a}*

Department of Energy Science & Engineering,
Daegu Gyeongbuk Institute of Science & Technology (DGIST),
50-1 Sang-Ri, Hyeongpung-Myeon, Dalseong-gun,
Daegu, 42988, Republic of Korea.
E-mail: sangarajus@dgist.ac.kr; Tel: +82-53-785-6413.

Experiment Section

Pre-treatment of Carbon fiber (CF)

The commercially available carbon fiber (CF) cloth was cleaned by sonication with acetone, ethanol, and DI water separately for 30 min. The cleaned CF was stirred for 1 h in the mixture of conc. H₂SO₄ (60 mL) and conc. HCl (120 mL). Afterward, 18 g of KMnO₄ was added to the above solution, and the temperature was raised to 45 °C. After maintaining for 1 h at the same condition, 500 mL DI water was added slowly under constant stirring. Finally, 30% H₂O₂ was added dropwise until no gas bubbles formed and the decolorization of KMnO₄. The pre-treated CF was washed with DI water several times and dried in a hot air oven. Finally, the chemically treated CF was sintered at 950 °C in a quartz tubular furnace under the flow of Ar/10% H₂ gas atmosphere.

Synthesis of Ni-MOF on Pre-treated CF

As reported in ref. S1, Ni-MOF on carbon fiber is synthesized using a modified solvothermal process. The solutions of 1 mmol Ni(NO₃)₂·6H₂O and 2 mmol 2-methylimidazole were dissolved in 48 mL of methanol separately and mixed slowly under constant stirring. The pre-treated CF was placed in the above solution and transferred to 110 mL Teflon-line autoclave container. Then, the autoclave was placed inside the hot air oven and heated for 6 h at 180 °C. After completing reaction conditions, the container was naturally cooled down to room temperature. The Ni-MOF grown on the CF (Ni-MOF@CF) was taken out from the reaction mixture, rinsed with methanol three times, and dried at 70 °C for overnight in the vacuum oven. The obtained Ni-MOF@CF was annealed in a quartz tubular furnace with a heating rate of 5 °C min⁻¹ under a gas flow of Ar atmosphere at 900 °C and named NiNC@CF. The powder form of Ni-MOF grown out of the CF was also collected from the bottom of Teflon, washed with DI water, dried, and annealed like Ni-MOF@CF for further characterizations and applications.

Synthesis of Nickel nanoparticle and NC

First, the powder of Nickel nanoparticles (NiNPs) was synthesized by heating the Ni-MOF to 900 °C and maintained for 3 h in an air atmosphere to completely remove the microporous carbon structures. Next, the obtained NiO was reduced to NiNPs by heating at 900 °C under the Ar/10% H₂ for 3 h.

The ZIF-8 was synthesized by following the procedure reported in the literature. The powder ZIF-8 was annealed with the heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ under a gas flow of Ar atmosphere at $700\text{ }^{\circ}\text{C}$ for 3 h

Materials Characterization:

The powder X-ray diffraction (PXRD) of MOF and its derivatives were collected from Rigaku, MiniFlex 600 using Cu $K\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). The morphology of NiNC@CF at different magnifications was observed using field emission scanning electron microscopy (FESEM) (Hitachi-S4800). A high-resolution transmission electron microscope (HRTEM, Hitachi HF-3300, 300 kV) was exploited to investigate the particle size, lattice fringes, and chemical composition of NiNC@CF. All the electron microscopic images were processed using digital micrographic software. The powder form of NiNC was used to record Raman spectra and FTIR spectra using Thermo Nicolet ALMEGA XR (Thermo Scientific) with 514 nm excitation lasers and Thermo Scientific/Nicolet Continuum IR microscope, respectively. Chemical composition and oxidation states of elements were obtained by performing the X-ray photoelectron spectroscopy (XPS) measurements using the Thermo-Scientific ESCALAB 250Xi apparatus.

Electrode preparation

After thermolysis, the NiNC@CF obtained from Ni-MOF@CF was used directly as an electrode without further NORR electrolysis treatment. In the case of control electrochemical measurements, the drop-cast method is used to fabricate the electrodes. The 5 mg of powder catalysts (NiNC, NC, NiNP, and commercial RuO_2) were mixed with 0.5 mL of ethanol and 0.1 mL of 5% Nafion to form a slurry. Then, the slurry was drop-casted onto pre-treated CF and dried at $70\text{ }^{\circ}\text{C}$ for 8 h (named here as d-NiNC, d-NC, d-NiNP, and RuO_2 , respectively). The loading of each catalyst on CF was maintained at $1.0 - 1.1\text{ mg cm}^{-2}$.

Electrochemical characterization

First, the PBS electrolyte was prepared by dissolving 10M Sodium dihydrogen phosphate and 5M of Disodium hydrogen phosphate in 500 mL DI water, and pH was adjusted to 7 by adding diluted HCl. The NiNC@CF, Ag/AgCl electrode (sat. KCl electrolyte), and commercially available graphite rod were used as the cathode, reference electrode, and anode. The electrochemical nitric oxide reduction reaction (NORR) was performed in the two compartments H-type cell, and the compartments were separated by the Nafion-212 membrane. Each compartment in the H-cell was filled with 60 mL of PBS electrolyte, and oxygen free

environment was maintained by purging with Ar gas for 1 h. Before performing NORR, the electrolyte in the cathodic compartment was saturated with NO gas by bubbling commercially available 100% NO gas for 30 mins at the rate of 1 sccm. To avoid further oxidation of NO to other oxides and solubility of atmospheric oxygen into the electrolyte, the headspace of the catholyte compartment was continuously filled with Ar gas during NORR performances. All electrochemical characterizations were performed by using Biologic instruments. Linear sweep voltammetry was recorded from 0.2V to 1.0 V vs. RHE at the scan rate of 0.5mV s⁻¹. The reduction potential was fixed with interval, and chronoamperometry (CA) experiments were performed based on the polarization curves. The reduction potential is converted into the reversible hydrogen electrode (RHE) using the following equation.

$$E_{RHE} = E_{Ag/AgCl} + 0.197V + 0.0591 \times \text{pH}$$

At the end of the NORR, the aliquots taken from the electrolyte were used to detect and quantify ammonia, NH₂OH, and N₂H₄ by using UV visible spectroscopy and NMR techniques.

In the case of two electrode prototype cell, the NiNC@CF cathode was coupled with commercial RuO₂ (anode). The polarization curves and CA were performed from 0.5 V to 3 V in a two-electrode system. In the long-term stability experiment, the CA was conducted by purging 100% NO gas continuously at the rate of 1 sccm for 5 h. The aliquots were collected at various time intervals and used for spectroscopy characterization. After the electrochemical performance, the electrocatalyst was collected and washed with DI for several times and dried. Then, the samples were used to conduct the post-electrocatalytic analysis by XRD, FESEM, and XPS.

Colorimetric techniques

Detection and quantification of NH₃ (indophenol blue method)

Ammonia synthesized by the electrochemical NORR process was detected and quantified by the indophenol method. In detail, 2 mL electrolyte obtained after the NORR process was mixed with 2 mL of 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate solution. Then, 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt% sodium nitroferricyanide solution were added into the above solution and mixed well. The solutions were kept under the dark for 2 h to complete indophenol blue formation. The formation of the indophenol blue complex was confirmed by using UV-visible spectroscopy (Carry 5000 UV-Vis-NIR) from the absorbance peak at the wavelength of 655 nm. To quantify NH₃, the calibration curves were obtained by

standard ammonium phosphate solution in various concentrations from 0 to 5 $\mu\text{g mL}^{-1}$ in 0.5 M PBS solution. The concentration to absorbance relation (i.e., $y = 0.324x + 0.0492$, $R^2 = 0.9996$) was evaluated from the standard calibration curves (**Fig. S15**)

Detection and quantification of N_2H_4 (Watt and Chrisp method)

In this method, a mixture of 5.99 g of p-dimethylaminobenzaldehyde and 30 mL of Conc. HCl was added into 300 mL ethanol and used as a colour reagent to determine the concentration of hydrazine in the electrolyte. 2 mL of electrolyte was taken out after the NORR process to mix with 5 mL of colour reagent. After 30 min, the solution was used to record the UV visible spectra. The peak at 455 nm in UV visible spectroscopy confirms the formation of N_2H_4 in the NORR process. The concentration to absorbance relation was evaluated from standard calibration curves (**Fig. S16**).

Determination of NH_2OH

The following colorimetric method was used to determine the hydroxylamine in the electrolyte. In brief, 1 mL of aliquot was taken out from the electrolyte and diluted with 1 mL of 0.05 M phosphate buffer solution (pH = 6.8) and 0.8 mL of DI water. Then, 0.2 mL of trichloroacetic acid, 1 mL of 8-quinolinol, and 1 mL of 1 M Na_2CO_3 solution were mixed with the above solution. Finally, the solution was kept boiling water under dark conditions for 1 min. The formation of a green colour complex and peak at 705 nm in UV-visible spectra confirmed the presence of hydroxylamine in the electrolyte. The calibration curves were obtained by recording UV-visible spectra for the various concentration of NH_2OH in PBS solution shown in **Fig. S17**.

NMR quantification of NH_3

The analyte used to detect NH_3 by the NMR measurements was composed of 400 μL of electrolyte mixed with 50 μL of freshly prepared 4 M H_2SO_4 and 50 μL of $\text{DMSO-}d_6$. Additionally, 100 μL of 2500 μM maleic acid was used as an internal standard reference. The linear plot (**Fig. S18**) between the concentration of ammonia and the area under the peak was calculated by recording the NMR spectra for standard ammonia phosphate in the PBS solution.

The yield rate of NH₃ and Faradic efficiency calculation:

The yield rate of ammonia from the NORR process was calculated by the following equation

$$\text{Yield rate} = \frac{C_{\text{NH}_3} \times V}{t \times a} \quad (\mu\text{mol cm}^{-1} \text{ h}^{-1})$$

Here,

C_{NH_3} = concentration of ammonia in PBS electrolyte (μmol)

V = total volume of the electrolyte in the cathodic compartment (ml)

t = duration of each chronoamperometry experiment (h)

a = geometric active area of the electrocatalyst (cm)

The faradic efficiency of each NORR process was evaluated by the following equation.

$$\text{Faradaic efficiency} = \frac{n \times F \times C_{\text{NH}_3} \times V}{Q \times 17} \times 100\%$$

Here,

n = number of electrons used to reduce NO molecule to NH₃

F = F is the Faraday constant (96485 s A mol⁻¹)

Q = total charge consumed to produce ammonia in PBS electrolyte.

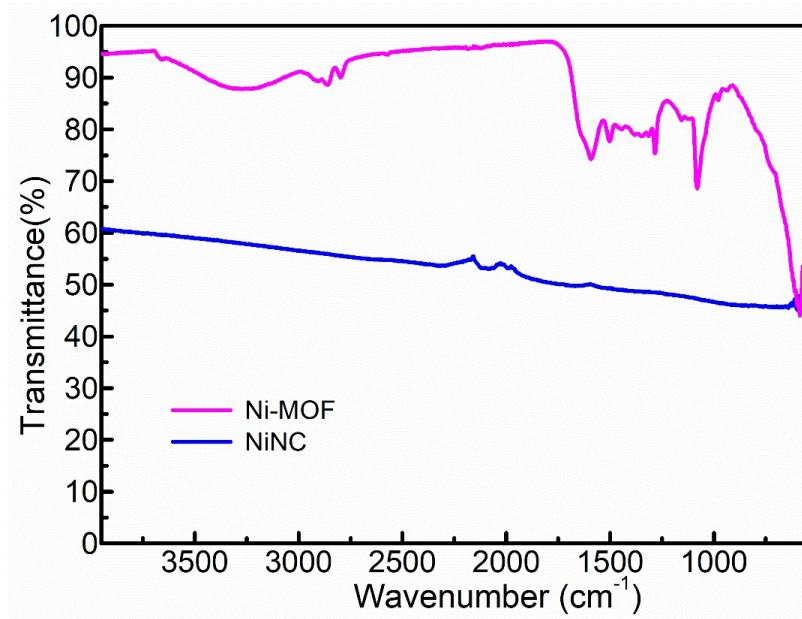


Fig. S1. FTIR Spectrum of Ni-MOF and NiNC.

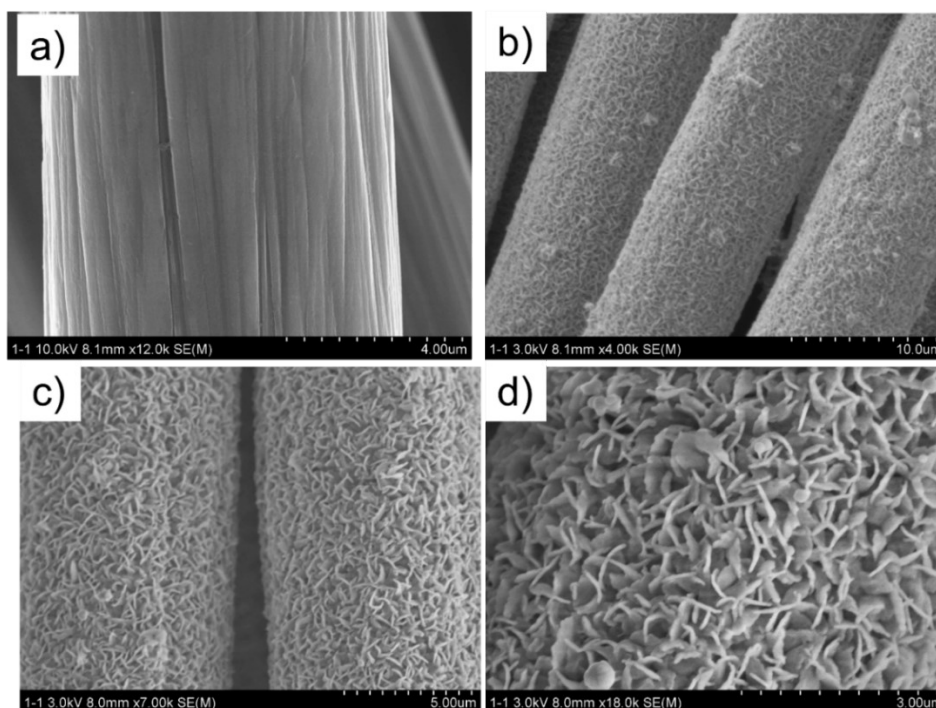


Fig. S2. (a) SEM images of pre-treated carbon fiber, (b-d) Low and high magnification FESEM images of Ni-MOF@CF.

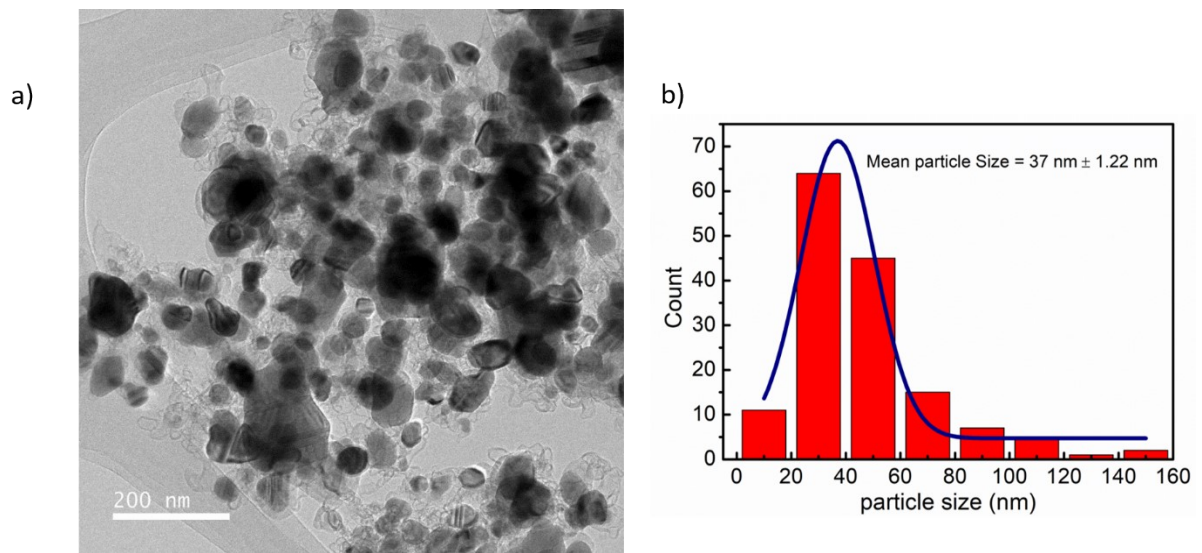


Fig. S3. (a) TEM image of NiNC@CF and (b) particle size distribution histogram graph.

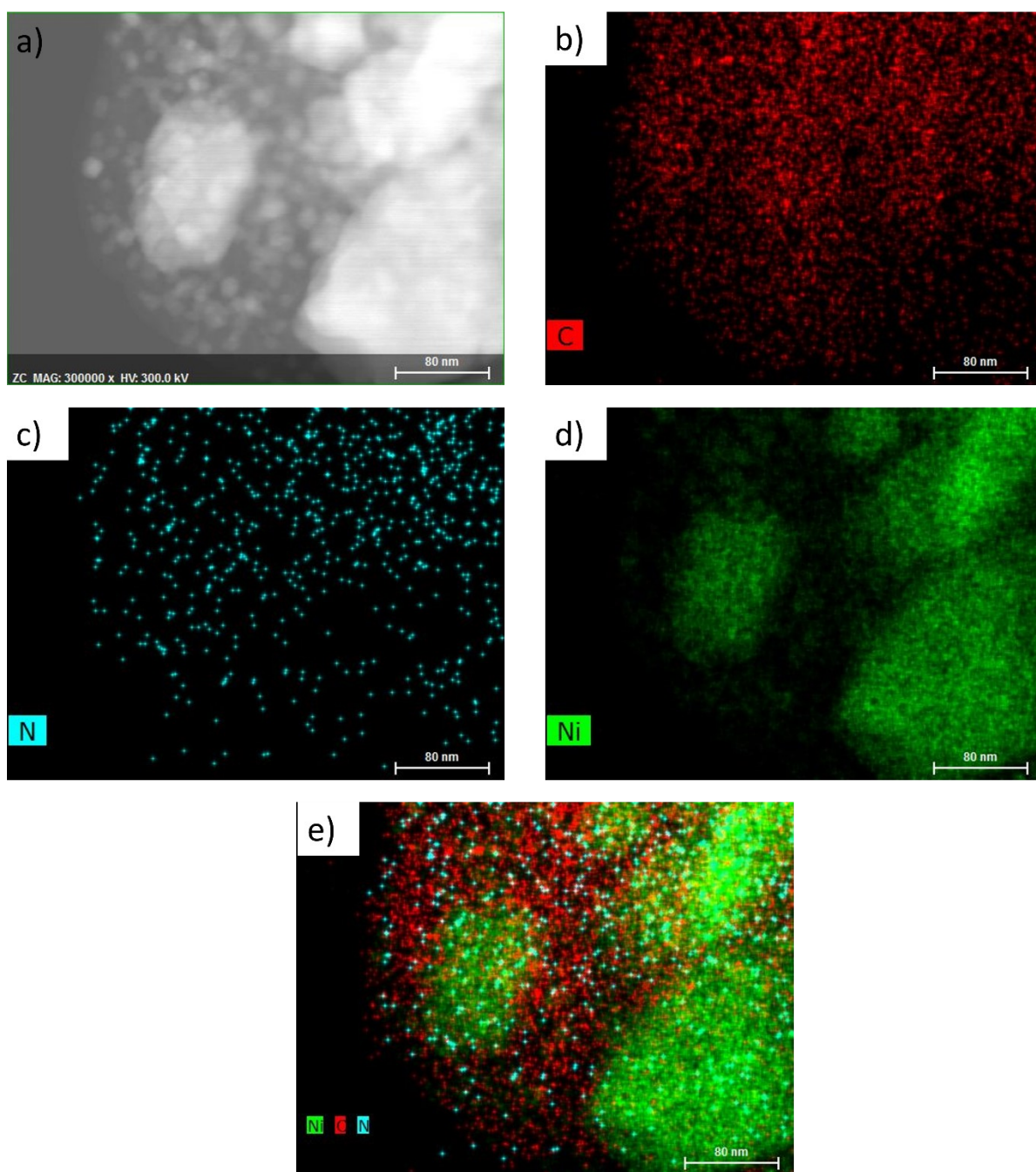


Fig. S4. (a) HAADF-STEM and (b-e) EDS elemental mapping of NiNC@CF.

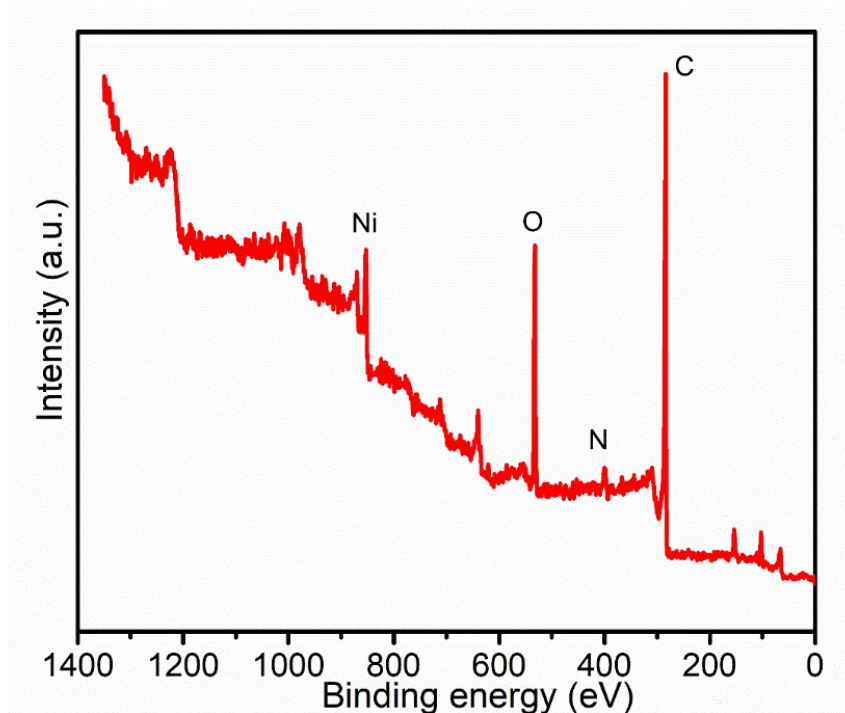


Fig. S5. The XPS survey spectra of NiNC@CF.

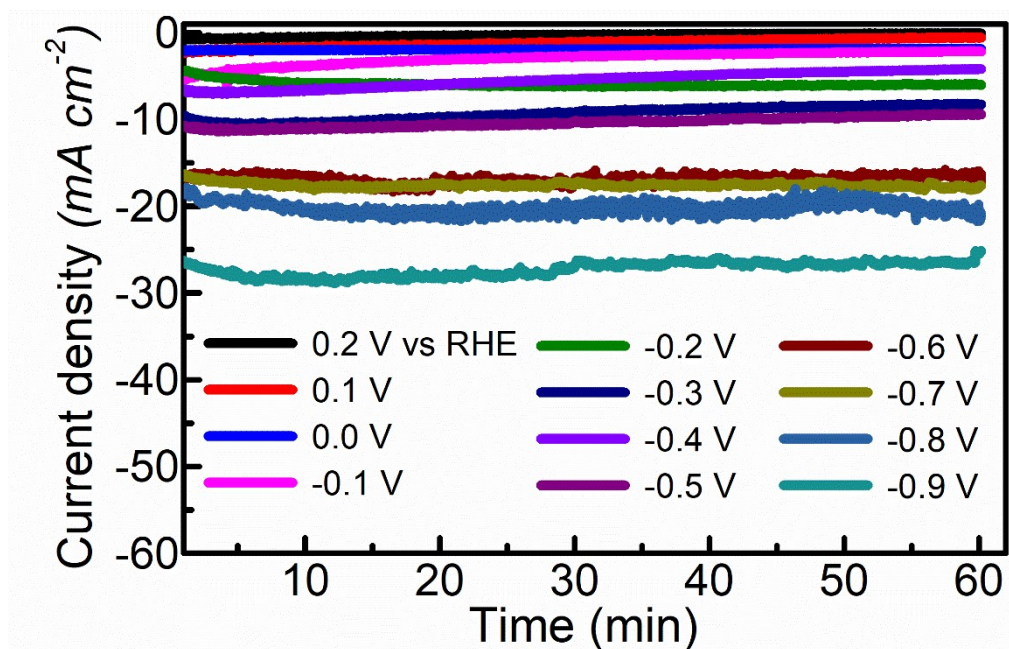


Fig. S6. Chronoamperometry experiments of NiNC@CF for 1 h NORR at -0.5 V vs. RHE.

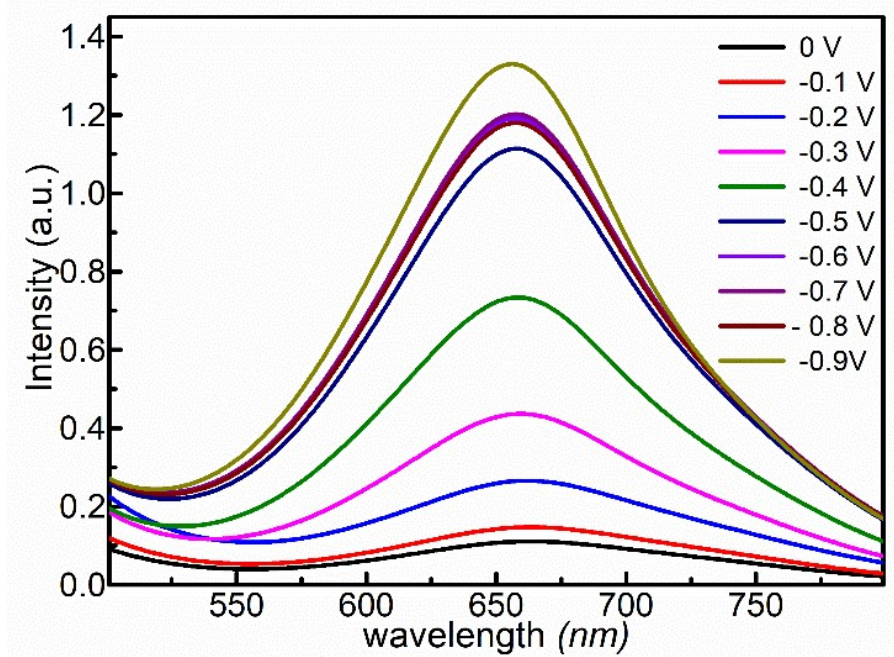


Fig. S7. UV- visible spectra of the electrolyte after 1 h of NORR at various potentials. [Before staining with indophenol indicator, the electrolytes were diluted with corresponding pristine electrolyte in a volume ratio of 1:7].

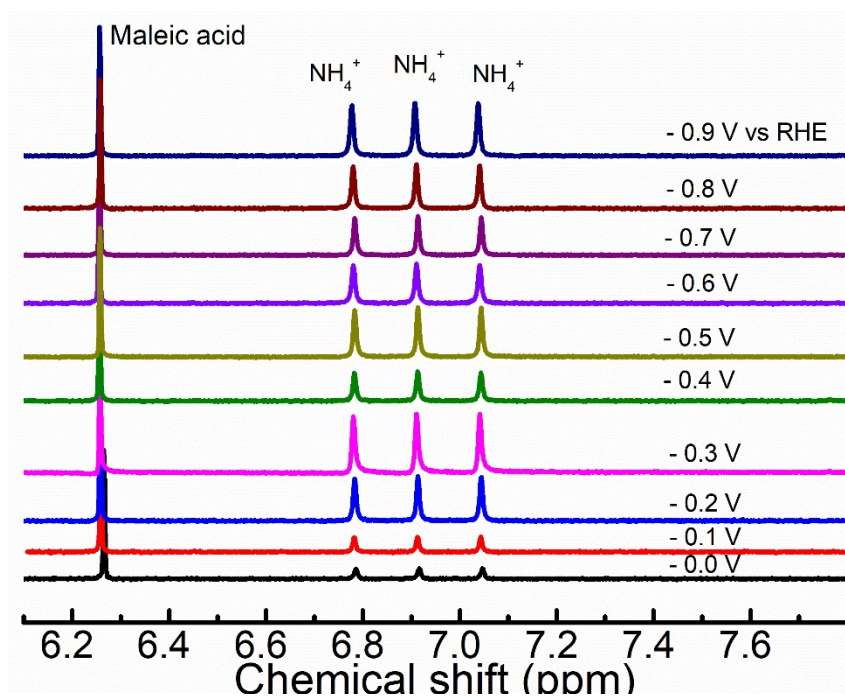


Fig. S8. ^1H NMR analysis of the electrolyte after NORR process at various potentials. [Before preparing the analyte for ^1H NMR spectra analysis, the electrolytes were diluted with corresponding pristine electrolyte in a volume ratio of 1: 4 for the potential ranges from -0.4 to - 0.9 V vs. RHE].

Table S1. Comparison of NH₃ and FE yield rate between UV-visible method and ¹H NMR technique for NORR at various potentials.

Potential (V) vs. RHE	UV vis		NMR	
	Yield rate of NH ₃ (μmol h ⁻¹ cm ⁻²)	FE (%)	Yield rate of NH ₃ (μmol h ⁻¹ cm ⁻²)	FE (%)
0	4.6	30.7	4.5	29.9
-0.1	7.8	46.0	6.5	37.5
-0.2	17.3	55.0	18.3	59.7
-0.3	31.2	71.2	30.3	69.0
-0.4	53.4	76.8	54.6	78.6
-0.5	94.4	87.3	95	88.5
-0.6	93.6	73.8	92	72.5
-0.7	94.4	65.6	90.3	62.7
-0.8	92	61.0	90.8	60.2
-0.9	107.6	53.4	106.6	53.0

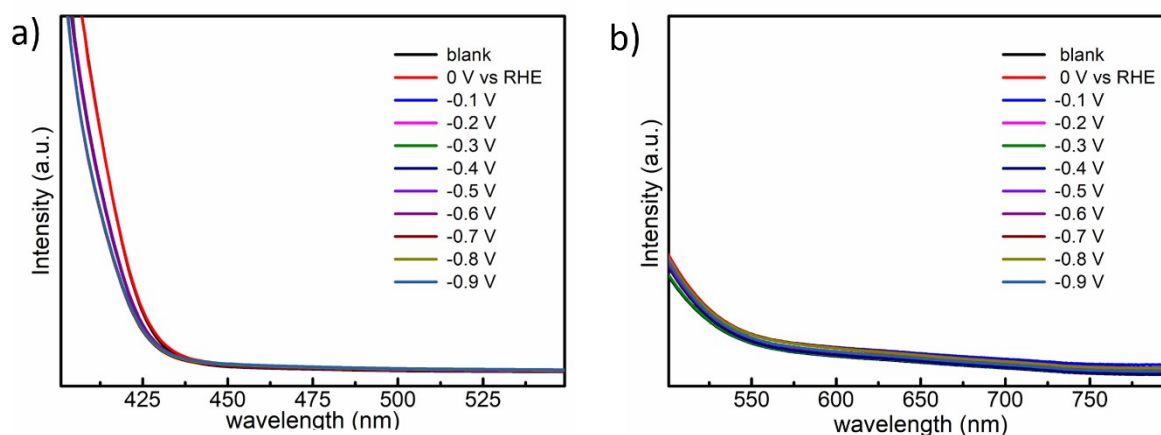


Fig. S9. UV-Visible absorption spectra of electrolyte aliquots by the watt and chrisp method for hydrazine (a) and hydroxylamine(b) after 1 h of NORR at various potentials.

Table S2. Electrocatalytic NORR performance comparison between NiNC@CF and other electrodes reported.

Electrocatalyst	Electrolyte/ complex agent	V vs RHE	Yield rate of NH ₃	FE (%)	References
NiNC@CF	0.5 M PBS	-0.5 V/ -0.9 V	94 108	84 52	This work
MnO array @ Ti mesh	0.2 M Na ₂ SO ₄	-0.8 V	27.5 × 10 ⁻¹⁰ mol s ⁻¹ cm ⁻²	82	<i>Materials Today Physics</i> , 2022, 22, 100586
Ni ₂ P array @ carbon paper	0.1 M HCl	-0.2 V	33.47 μmol h ⁻¹ cm ⁻²	76.9	<i>J. Mater. Chem. A</i> , 2021, 9, 24268-24275
NiO nanosheet	0.1 M Na ₂ SO ₄ 0.2 0.5 mM Fe ²⁺ - EDTA	-0.6 V	2130 μg h ⁻¹ cm ⁻²	90	<i>Chem. Commun.</i> , 2021, 57, 13562-13565
MoS ₂ @GF	0.1 M HCl Fe ²⁺ Sodium benzoate	-0.7 V	99.6 μmol cm ⁻² h ⁻¹	76.6	<i>Angew. Chem. Int. Ed.</i> 2021, 60, 25263–25268
Ag	1 M HClO ₄ / 50 mM Fe ²⁺ complex	-0.165 V	0.28 mol cm ⁻² h ⁻¹		<i>ACS Energy Lett.</i> , 2020, 5, 3647-3656
Cu-Foam	0.25 M Li ₂ SO ₄	-0.9 V	517.1 μmol cm ⁻² h ⁻¹	93.5	<i>Angew. Chem. Int. Ed.</i> , 2020, 59, 9711–9718
Cu-Foil		-0.9 V	95 μmol cm ⁻² h ⁻¹	-	
Pt-Foil		-0.9 V	99.4 μmol cm ⁻² h ⁻¹	-	

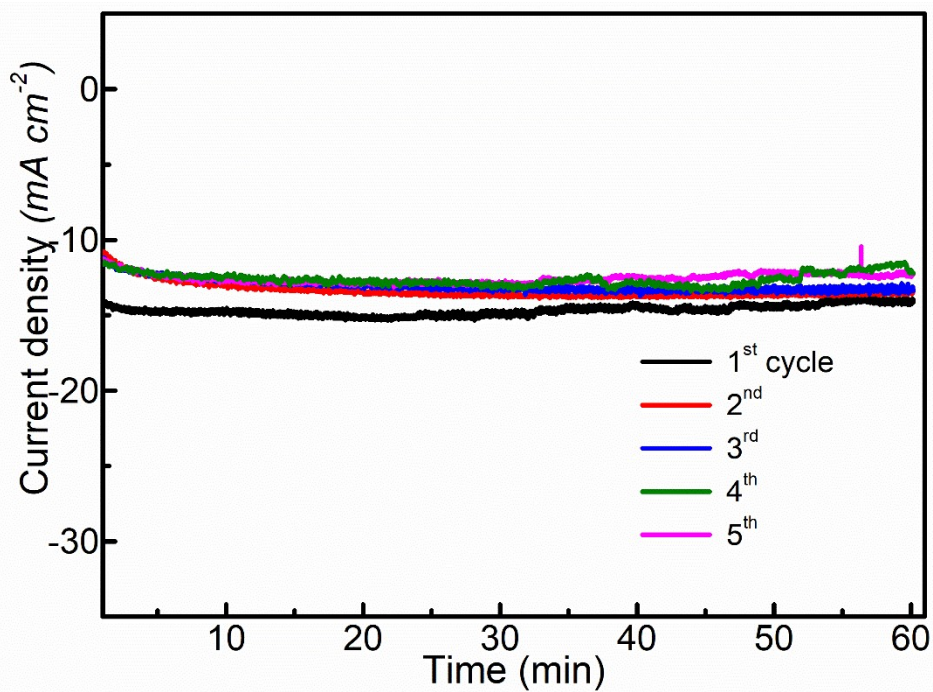


Fig.10. Chronoamperometry test of NiNC@CF for 5 cycles of NORR at -0.5 V vs. RHE.

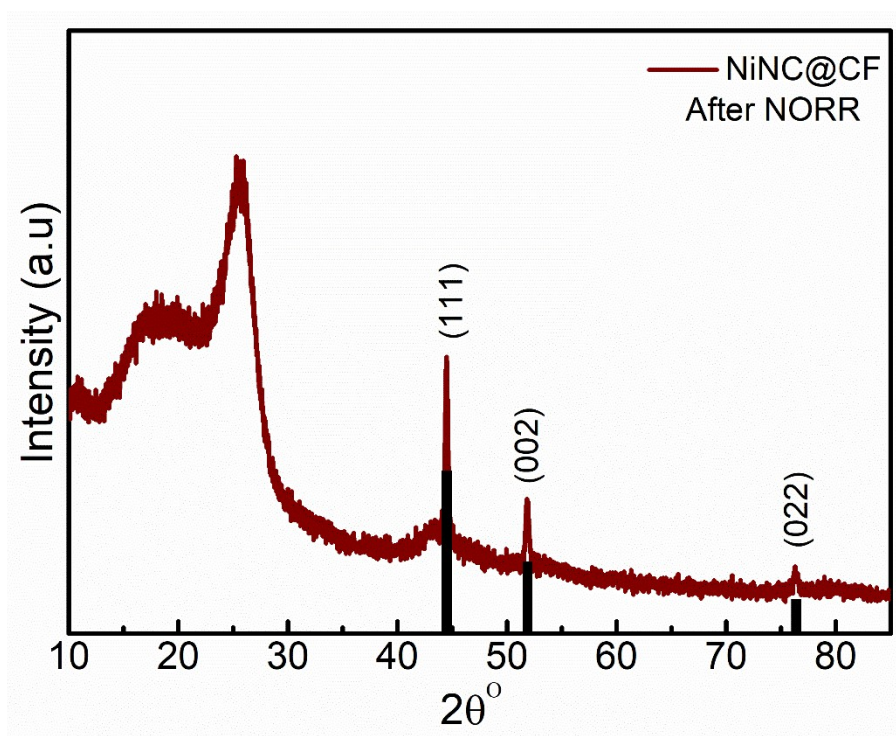


Fig. S11. XRD pattern of NiNC@CF after extended NORR performance.

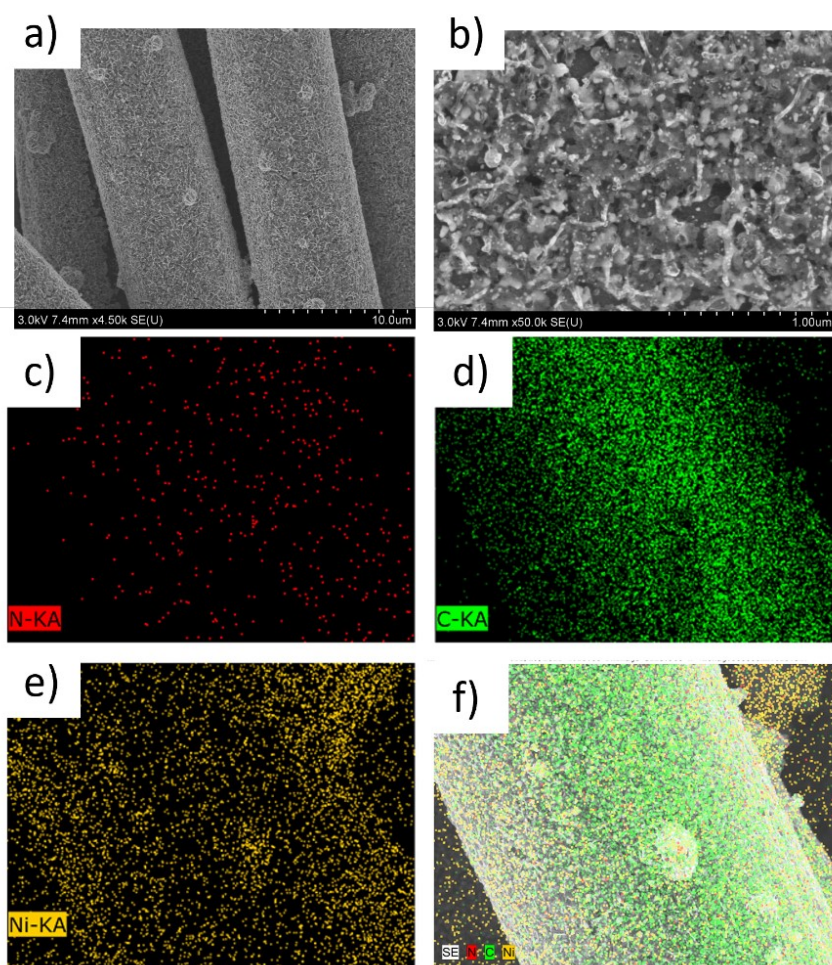


Fig. S12. (a) Low and (b) high magnification FESEM and (c-f) their corresponding EDS elemental mapping of NiNC@CF after NORR.

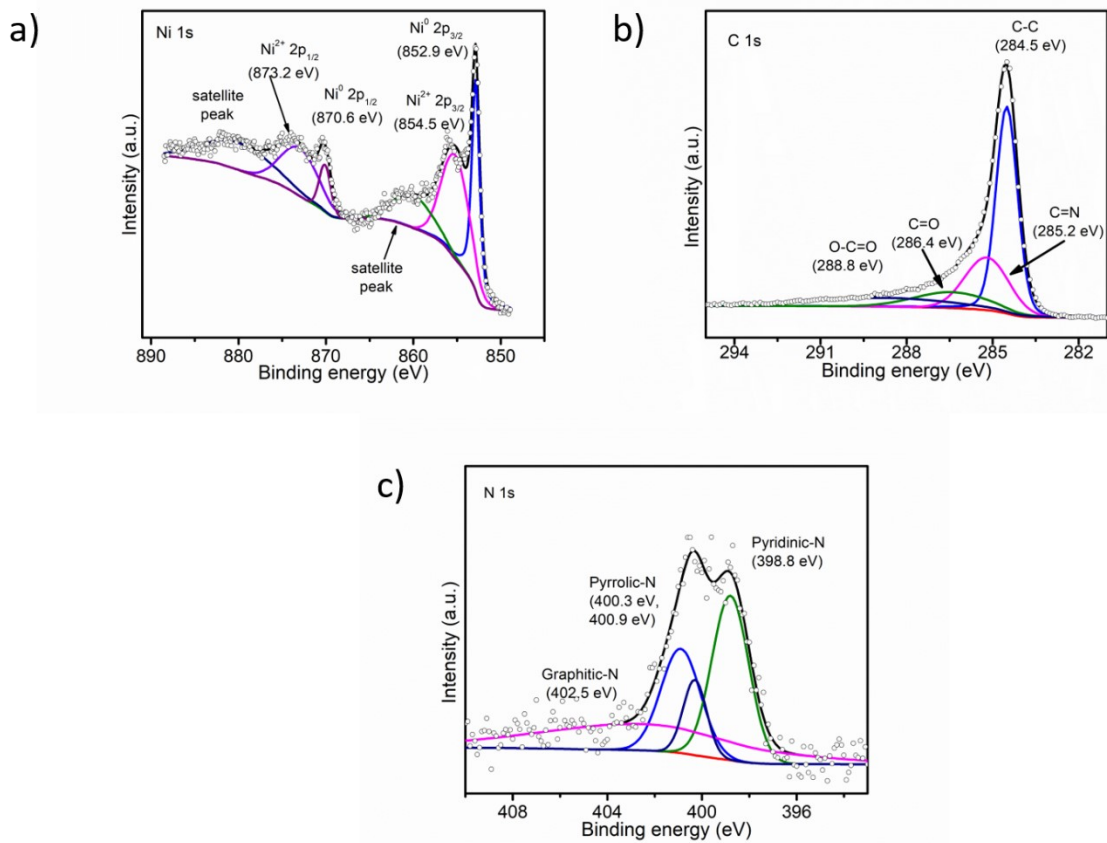


Fig. S13. High-resolution XPS spectra of (a) Ni, (b) C, and (c) N of NiNC@CF electrode after NORR process.

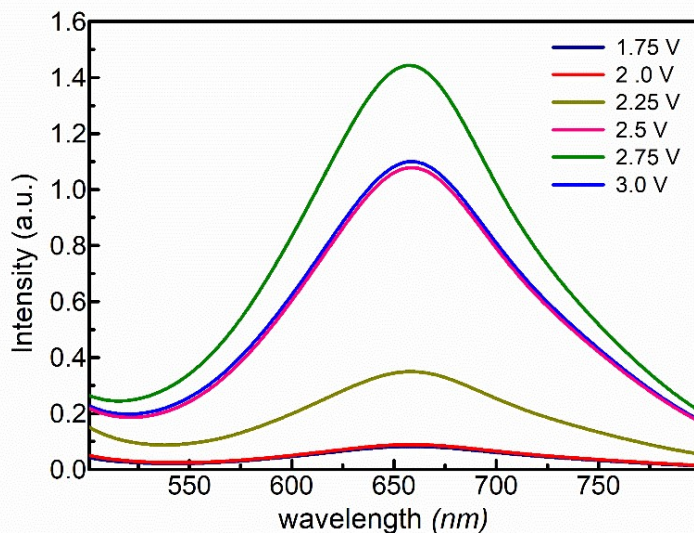


Fig. S14. UV-visible spectra in the electrolyte after 1 h electrolysis at a series of potential in the full cell system.

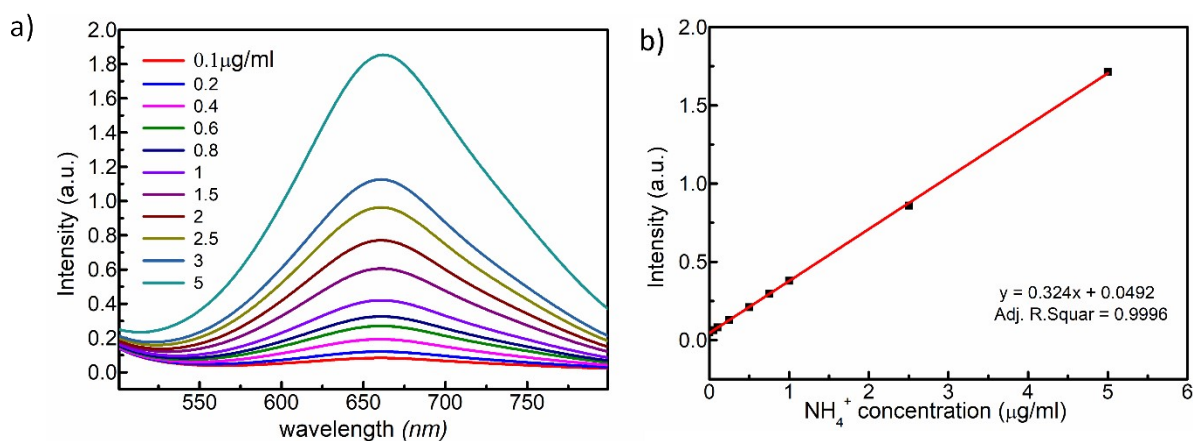


Fig. S15. Standard calibration of NH_3 by indophenol method. (a) UV- Visible spectra of standard NH_4Cl solutions in 0.5M PBS electrolyte. (b) Linear relation of concentration of NH_4^+ vs. absorbance at 655 nm.

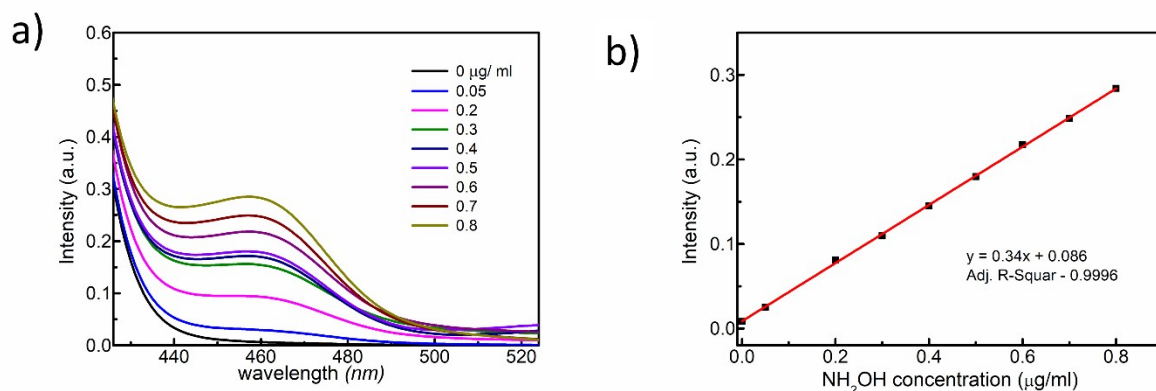


Fig. S16. (a) UV-visible absorption spectra of Watt and Chrisp assays with various concentration of hydrazine solutions and (b) their corresponding calibration curve.

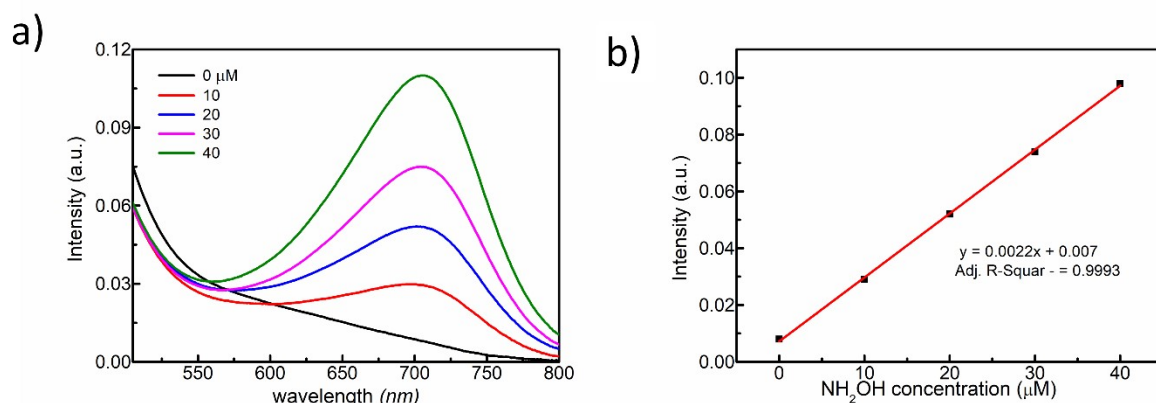


Fig. S17. (a) UV visible spectra of hydroxylamine and (b) estimated calibration curve at various concentrations.

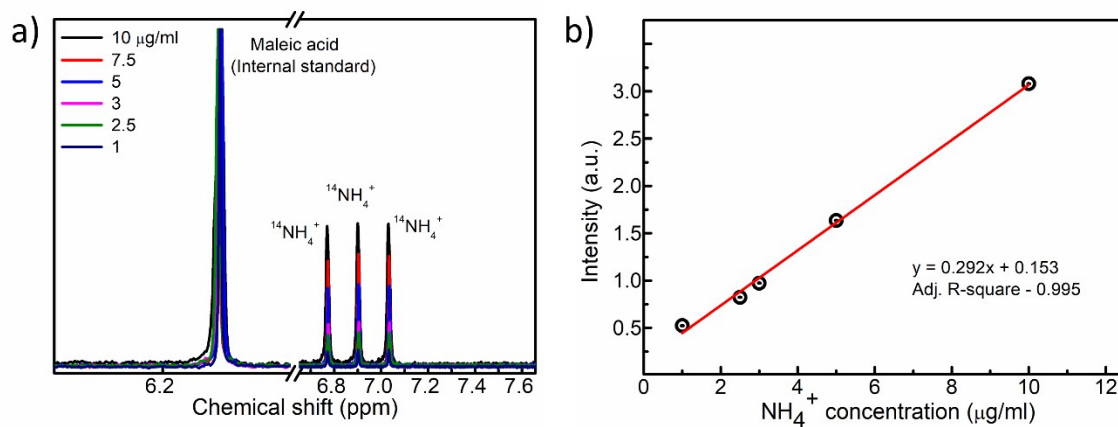


Fig. S18. (a) ^1H NMR spectra of NH_4^+ solution in various concentrations of 1 to 10 microgram/ml. (b) linear calibration curves derived from the peak intensity of NH_4^+ in the NMR spectra.

References

- S1. M. Ding, J. Chen, M. Jiang, X. Zhang and G. Wang, *J. Mater. Chem. A*, 2019, **7**, 14163-14168.