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rsc.li/materials-aNickel nanoparticles wrapped in N-doped carbon nanostructures for efficient electrochemical reduction of NO to NH₃†Tamilselvan Muthusamy, Sridhar Sethuram Markandaraj
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Production of ammonia (NH₃) from flue gas (*i.e.*, NO) *via* the electrocatalytic route has been considered a promising approach for rejuvenating the environment over the conventional methods. MOF-derived zero-valent nickel nanoparticles wrapped with nitrogen-doped carbon nanostructures (NiNC) were successfully grown on a carbon fiber (CF). The NiNC@CF catalyst delivered an NH₃ yield rate of 94 μmol h⁻¹ cm⁻² with significantly high faradaic efficiency (87%) at -0.5 V vs. RHE. Coupling with an OER catalyst in a full cell system produces 88 μmol h⁻¹ cm⁻² of NH₃ with long-term stability.

Ammonia (NH₃) is a building block and vital chemical in modern chemical industries such as fertilizer, pharma, and textile.¹⁻³ Due to the versatile application of NH₃, it has been produced more than 150 Mt worldwide by different strategies.⁴ The old Haber Bosch process is the most successful method to produce NH₃ on a large scale.⁵ However, this NH₃ production method involves high temperature and pressure and the emission of greenhouse gases. Recently, the electrochemical synthesis of NH₃ from H₂ and abundant natural N₂ in solid oxide fuel cells and electro reduction of N₂ in an aqueous electrolyte is gaining tremendous attention because of their zero-emission of carbonaceous gases.^{6,7} However, improper solubility of N₂ in the electrolyte, higher activation energy barrier, and competitive HER in the aqueous electrolytes are still formidable challenges in the large-scale production of NH₃.⁸ Other than abundant N₂, few nitrogen-based oxides such as NO₂, N₂O, and NO can be used as a source of NH₃ production *via* the electrochemical reduction method.⁹ NO is one of the major by-products of the high-temperature combustion engines and coal cracking process.¹⁰ Since the lower concentration in the atmosphere, NO is not considered hazardous to health. However, if NO concentration increases in the atmosphere, it will lead to environmental deterioration.¹¹ Compared with N₂,

NO molecules display lower bonding energy and relatively high solubility in aqueous electrolytes.¹²⁻¹⁴ Due to this, valuable products such as N₂H₄, NH₂OH, NH₃ and harmless N₂ can be directly synthesized from NO gas *via* the electrochemical NO reduction reaction (NORR) method.¹⁵ In addition, this process assists in restoring the pristine nature of the environment.

Few transition metals, noble metals, single-atom catalysts, and metal sulfides have been explored as electrocatalysts in the field of NORR.¹⁶⁻²⁴ Among the transition metals, Fe, Ag, and Cu nanoparticles and foils have shown promising results in the electrochemical synthesis of NH₃ from NO in an aqueous electrolyte.^{19,21,25} However, due to NO molecule corrosive nature, the electrocatalyst, particularly metal nanoparticles, undergo degradation and dissolution in the electrolyte during the NORR process, limiting the efficiency of electrocatalyst during the long term NORR process.²⁵ Various strategies have been explored to enhance the chemical stability of the electrocatalyst and increase NH₃ yield. For example, using highly diluted NO gas enhances the yield of NH₃ drastically, but still, it displays poor long-term stability.²⁵ In some cases, introducing metal complexing agents in electrolysis improves the solubility of NO in the electrolyte, thus enhancing the electron transport and slowing down the dissolution of catalysts.^{19,20,26,27} However, using metal complexes in electrolysis will interfere with the determination of NH₃ yield by a feasible colorimetric method. To overcome the above issues, chemically stable metal/metal composite electrocatalysts that can withstand a NO saturated aqueous electrolyte are necessary.

In this study, we explored the NC-wrapped zero-valent nickel nanoparticles on the carbon fiber (CF) and used it as a stable and efficient electrocatalyst for the NORR process. NiNC@CF possesses a strong interaction between the CF and active catalyst and chemical stability in the NO saturated electrolyte. It attains a maximal faradaic efficiency of 87% with an NH₃ yield rate of 94 μmol h⁻¹ cm⁻² under the 100% NO gas saturated electrolyte. A single cell set-up was demonstrated by coupling NORR and the anodic OER. The cell shows an NH₃ yield rate of 27 μmol h⁻¹ cm⁻² with 80% faradaic efficiency. Thus, it displays

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a high performance with long-term stability in the NORR process.

A binder-free NiNC@CF electrode was synthesized by a two-step process (Fig. 1a), as described in ESI.† In Fig. 1b, the XRD peaks appeared at 44.8, 52.1, and 76.5° corresponding to the crystallographic planes of (111), (002), and (022) of metallic Ni (PDF no. 98-005-2231). In the case of NiNC (powder), a peak at 26° was observed, which confirms the formation of low crystalline carbonous nanostructures along with metallic Ni. The FT-IR spectra show no prominent peaks in the NiNC catalyst compared to Ni-MOF (Fig. S1†). These results indicated the complete decomposition of organic functional groups in Ni-MOF frame structures and the conversion into carbonous microstructures during the pyrolysis process.

Ni-MOF@CF possesses ordered high dense nanoflakes in nature, as shown in FESEM (Fig. S2†). However, the FESEM images of NiNC@CF presented in Fig. 1c and d confirm that the initial morphology of Ni-MOF@CF nearly collapsed after thermal pyrolysis. The Ni nanoparticles were still well dispersed over porous N-doped carbon microstructures with a uniform coating on the CF surface. The elemental composition and mappings of NiNC@CF are shown in Fig. 1e. The elemental mapping results ensure the uniform dispersion of Ni, C, and N throughout the surface of CF, indicating a high distribution of

NiNC nanoparticles. The HRTEM image of NiNC@CF (Fig. 1f and S3†) further confirms the even dispersion of Ni nanoparticles with an average size of 37 nm. Each of the nanoparticles has well-defined surface facets and is encapsulated with layers of carbon structures.

In addition, it is well connected by ultrathin graphene layers shown in Fig. 1f. The interlayer distance of 0.203 nm obtained from the HRTEM image represents the lattice fringe plan of (111) from Ni nanoparticles (Fig. 1g). The distance between each layer in the carbon structure is around 0.33 nm (Fig. 1h), which confirms the graphitic nature of carbon. The HAADF-STEM and elemental mapping of NiNC@CF conform to the Ni nanoparticle wrapped with N-doped carbon nanostructures (Fig. S4†). The ratio between the Ni, C, and N atoms is 72 : 27 : 1, as evaluated by C, H, N, and S elemental analysis.

The nature and degree of graphitization of the N-doped carbon microstructure in the NiNC catalyst were studied by Raman spectroscopy. In Fig. 2a, the characteristic sp^2 hybridization peaks appeared at 1330 and 1590 cm^{-1} , corresponding to the D and G bands. The intensity ratio between D and G bands (I_D/I_G) is around 0.85, indicating a high degree of graphitization in N-doped carbon nanostructures. In addition, a broad peak appeared at 2671 cm^{-1} , suggesting the presence of a few layers of graphene in NiNC@CF. It was further confirmed by the HRTEM results.

The oxidation states and survey XPS spectra reveal the presence of Ni, C, N, along with surface absorbed O atoms in NiNC@CF (Fig. S5†). High-resolution XPS spectra (Fig. 2b) of Ni 2p in NiNC@CF show high-intensity peaks at 852.9 and 870.6 eV, representing the spin-orbit doublet ($2p_{3/2}$ and $2p_{1/2}$) of zero-valent Ni atoms. This finding confirms the existence of metallic Ni from Ni-MOF. In addition, low-intensity peaks at 854.5 and 873.1 eV are also observed, and it is assigned to Ni^{2+} ions from Ni-N co-ordination and surface oxidized Ni atoms. There are two satellite peaks of Ni atom also observed at the

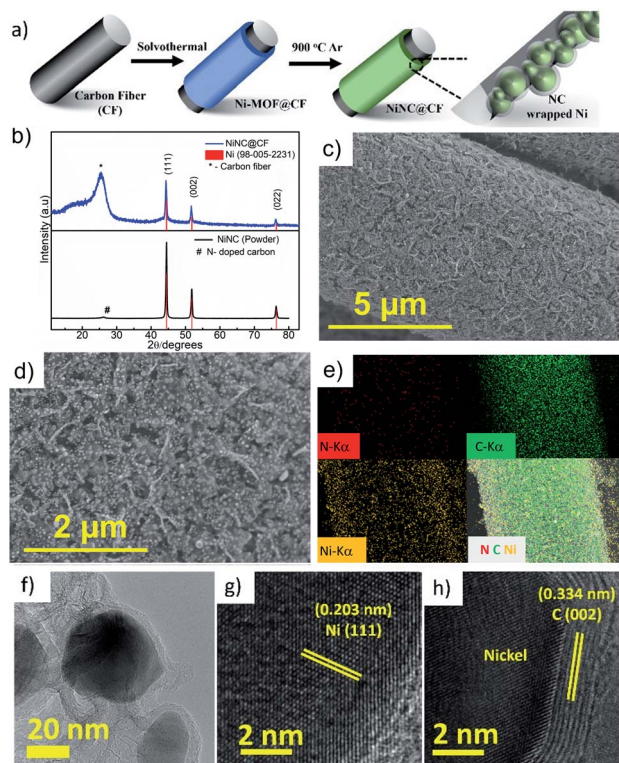


Fig. 1 (a) Schematic of the synthesis of NiNC@CF electrocatalyst. (b) XRD pattern of NiNC@CF and NiNC (powder) along with reference pattern, (c) low and (d) high magnification FESEM images of NiNC@CF, (e) FESEM elemental mapping for NiNC@CF, (f)–(h) TEM and HRTEM of NiNC@CF. The lines in (g) and (h) represent the Ni and hexagonal C lattice fringes.

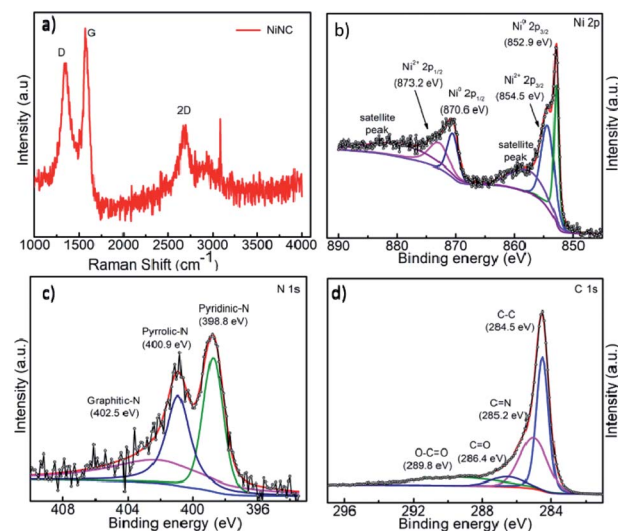


Fig. 2 (a) Raman spectra of NiNC (powder). High resolution XPS spectra of (b) Ni 2p, (c) N 1s, and (d) C 1s.



binding energies of 861 and 879 eV. By deconvoluting the core level N 1s (Fig. 2c) spectra, three peaks were obtained at 398.8, 400.9, and 402.5 eV, corresponding to the pyridinic, pyrrolic, and graphitic nature of N atoms, respectively. The high-resolution C 1s can be fitted into four characteristic peaks of carbon from various co-ordination carbon species, such as C–C (284.5 eV), C=N (285.5 eV), C=O (286.4 eV), and O–C=O (289.8 eV) (Fig. 2d).

Using the NiNC@CF catalyst as a cathode, the electrochemical synthesis of NH_3 from the dissolved NO gas (100%) was carried out in the PBS electrolyte (pH = 7). Fig. 3a demonstrates the LSV curves of NiNC@CF and bare CF cathode in NO and Ar saturated electrolytes. In the case of the NO saturated electrolyte, NiNC@CF shows a significant current response starting from 0.1 V vs. RHE, suggesting the reduction of NO gas in the electrolyte. At the higher negative potentials, the current density increases drastically, which is contributed to the high degree of NORR activity and competitive HER process. In contrast, the bare CF (current collector) shows poor electrocatalytic activity towards the NO reduction process (Fig. 3a).

The chronoamperometry (CA) curves of each electrocatalyst under various polarization potentials are acquired and plotted in Fig. S6†. At the end of a 1 h NO reduction test, the electrolyte aliquots were used to detect and quantify NH_3 by the standard indophenol method (see details in ESI†). The absorbance peak at 655 nm in UV visible spectra confirms the formation of NH_3 .²⁸ From the results (Fig. S7†), NiNC@CF delivered the highest yield rate of NH_3 at -0.9 V vs. RHE with a faradaic efficiency of 53% (Fig. 3b). However, it displays maximum FE at -0.5 V vs. RHE with a relatively lower NH_3 yield rate ($94 \mu\text{mol cm}^{-2} \text{h}^{-1}$).

In addition, a lower polarization potential (more positive vs. RHE) will be favorable to forming N_2O gas products from NO gas. Moreover, the HER reaction becomes more prominent at the higher polarization potential (more negative vs. RHE).²⁹ The formation of NH_3 is further confirmed and quantified *via* ^1H NMR spectroscopy. The triplet peak in the NMR spectra (Fig. S8†) confirms the presence of NH_3 in the electrolyte.³⁰ The FE and yield values obtained from the NMR calibration curves nearly match the value calculated by the UV-visible spectroscopy technique (vs. ESI†). The electrolyte was further examined to detect other NO reduced products such as NH_2OH and N_2H_4 by the NORR process. In the UV-visible spectra (Fig. S9†), the absence of the absorbance peak at NH_2OH (455 nm) and N_2H_4 (705 nm) ruled out the formation of NH_2OH and N_2H_4 , respectively.^{31,32} In Ar-saturated electrolyte (without NO), a negligible amount of NH_3 was detected at -0.5 V vs. RHE (Fig. 3c). This observation ensures that dissolved NO gas in the electrolyte is the only source for the formation of NH_3 during NORR. From the above finding, it can be concluded that the NC-wrapped NiNC@CF electrocatalyst delivered a superior NH_3 yield rate in an aqueous medium compared to reports in NRR and NORR processes (Table S2†).

The NiNC@CF electrode consists of various components such as Ni nanoparticles (NiNPs), N-doped carbon nanostructures (NC), and carbon fibre (CF). To understand the origin of the catalytic activity, each component was obtained, and their corresponding electrodes were fabricated using the drop-cast method (named as d-NiNP and d-NC, see details in ESI†). For better comparison, the NiNC (d-NiNC) electrode was also fabricated by the drop-cast method. The catalytic activity of controlled electrodes was tested using the LSV and CV. Based on the LSV (Fig. 3c), the current response in the NORR activity increases in the order: d-NC < d-NiNC < d-NiNP. From CA experiments (Fig. 3d and e), the d-NiNP electrode delivered a higher rate of ammonia yield than that of the d-NC electrode. The faradaic efficiencies were relatively comparable in both d-NiNP and d-NC electrodes. However, d-NiNP displays poor electrochemical stability, which might be due to the corrosion of NiNP from the electrode into the electrolyte during NORR (Fig. 3e). In the case of d-NiNC, the ammonia yield rate and FE is higher than d-NC and it delivered stable electrochemical performance than d-NiNP. The controlled experiments concluded that Ni nanoparticles mainly act as active sites for NO to NH_3 reaction and the porous N-doped carbon microstructures hinder the degradation and dissolution of Ni nanoparticles into the electrolyte. In addition, unique core-shell-like arrangements in the NiNC catalyst display synergism between the metallic Ni and N-doped nanostructures, enhancing electrocatalytic activity and chemical stability. Among all the electrodes, NiNC@CF displays relatively excellent NORR activity, which is attributed to the better electron transport between the catalyst and CF support and chemical stability.

The long-time stability of NiNC@CF was demonstrated by subjecting the electrocatalyst to five consecutive cycles (Fig. S10†). The faradaic efficiency of each cycle is maintained nearly the same (Fig. 3f). However, there is a slight loss in the rate of NH_3 yield. Thus, it might be attributed to the aggregation

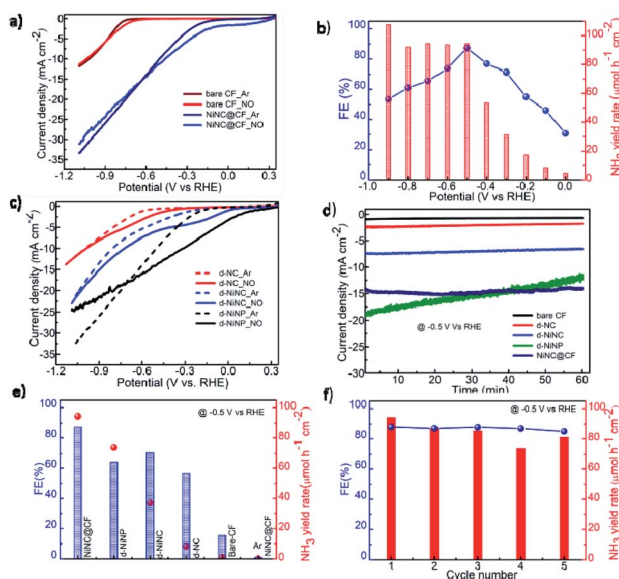


Fig. 3 (a) LSV curves of NiNC@CF and bare CF in Ar and NO saturated 0.5 M PBS. (b) NH_3 yield and FE of NiNC@CF in the 0.0 to -0.9 V vs. RHE after 1 h of NORR. (c) LSV curves of various electrodes in Ar- and NO saturated 0.5 M PBS electrolyte. (d) CA of various electrodes for NORR at -0.5 V vs. RHE. (e) Comparison of FE and NH_3 yields on various electrodes after 1 h of NORR (f) long term stability of NiNC@CF electrode at -0.5 V vs. RHE.



and slight detachment of the catalyst from the CF surface during repeated NORR and the cleaning process after each cycle. After NORR performance, the crystallinity, morphology, and chemical stability of NiNC@CF were analyzed by the XRD, SEM, and XPS techniques. In Fig. S11,[†] the characteristic peaks at 44.8, 52.1, and 76.5° in the XRD pattern confirm the retention of the metallic Ni state. In the case of morphology, a slight agglomeration in the electrocatalyst surface was observed in Fig. S12.[†] However, the elements of the NiNC@CF catalyst were still uniformly distributed on the CF even after extended NORR performances. From the core level XPS spectra (Fig. S13[†]), no significant changes in composition and chemical states are observed in NiNC@CF except in N 1s XPS spectra. After deconvoluting the N 1s XPS peak, one extra peak was observed at 399.9 eV, and it was assigned to the pyrrolic-N atom. The evaluation of the new peak of the pyrrolic-N atom is attributed to the reduction of the negative charge nitrogen atom in the NiNC@CF catalyst or interaction of some pyrrolic-N with NO molecule during the NORR process.^{33,34} The findings from the post electrocatalytic analysis indicate that NC layers on the Ni nanoparticles hinder the corrosion and enhance the chemical stability of NiNC@CF during the NORR process.

A prototype two-electrode (NORR/OER) electrolyzer was constructed in the H-cell by coupling commercial RuO₂ as an anode and NiNC@CF as a cathode. The typical non-iR compensated LSV curves are shown in Fig. 4a. The onset potential for NH₃ and O₂ formation was observed at 1.2 V. To evaluate the performance of the full cell, a series of CA were executed at a particular potential interval (Fig. 4b). From the UV-visible spectra (Fig. S14[†]), the potential dependent FE and NH₃ yield rates were calculated. Fig. 4c shows that a noticeable NH₃ starts producing at 1.75 V and the NH₃ yield rate and FE increase linearly along with applied potential. At 2.75 V, it delivered 27 μmol cm⁻² h⁻¹ of NH₃ with the highest FE (80%). Beyond 2.75 V, there is a significant loss in FE and yield rate, and it is attributed to the competitive HER process. The durability test of the NiNC@CF cathode in the full cell electrolyzer was performed by the CA over an extended period at 2.75 V. The

results in Fig. 4d showed a stable current density throughout electrolysis. It disturbed the nearly identical FE and yield rate of NH₃.

In summary, NiNC@CF was employed as a highly durable and efficient electrocatalyst for the efficient NORR process. It delivered a high performance of reducing NO to NH₃ (94 μmol h⁻¹ cm⁻²) with 87% faradaic efficiency at -0.5 V vs. RHE. In addition, NiNC@CF, applied as an OER catalyst in a full cell system, exhibits 27 μg h⁻¹ cm⁻² NH₃ yield with a FE of 84% and appreciable long-term stability. This electrochemical study on Ni wrapped in carbon microstructures unveils the stable catalytic activity during NORR and paves a new way to explore metal-carbon microstructures for NORR electrolyzers.

Conflicts of interest

There are no conflicts to declare.

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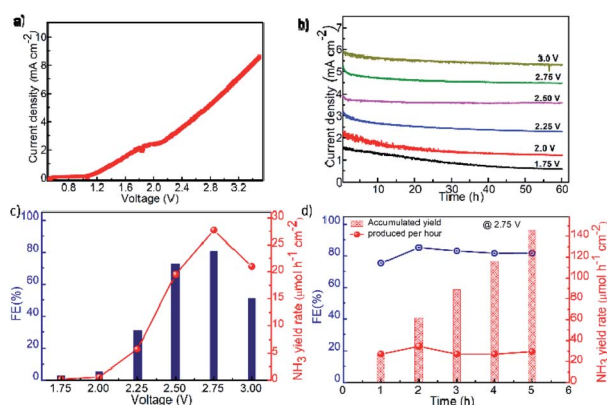


Fig. 4 (a) A single cell polarization curve in NO saturated 0.5 M PBS. (b) Chronoamperometry and (c) their corresponding FE and NH₃ yields at the various potential for 1 h of electrolysis. (d) Durability test of the NiNC@CF in the full cell system.



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