Chemical Vapor Deposition-Grown Nickel-Encapsulated N-Doped Carbon Nanotubes as a Highly Active Oxygen Reduction Reaction Catalyst without Direct Metal–Nitrogen Coordination

Dipsikha Ganguly,†‡ Ramprabhu Sundara,*†‡ and Kothandaraman Ramanujam*‡

†Alternative Energy Nanotechnology Laboratory, Nano Functional Materials Technology Centre (NFMTC), Department of Physics, and ‡Clean Energy Laboratory, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

ABSTRACT: Nickel-encapsulated nitrogen-doped carbon nanotubes (Ni–TiO2–NCNTs) are synthesized via chemical vapor deposition by thermal decomposition of acetylene with acetonitrile vapor at 700 °C on the Ni–TiO2 matrix. TiO2 is used as a dispersant medium for Ni nanoparticles, which assists in higher CNT growth at high temperatures. A reference catalyst is made by following the similar procedure without acetonitrile vapor, which is called a Ni–TiO2–CNT. Acid treatment of these two catalysts dissolved Ni on the surface of CNTs–NCNTs, producing catalysts with enhanced surface area and defects. The transmission electron microscopy—energy-dispersive X-ray spectra analysis of acid-treated version of the catalysts confirmed the presence of encapsulated Ni. Oxygen reduction reaction (ORR) activity of these catalysts was analyzed in 0.1 N KOH solution. Among these, the acid-treated Ni–TiO2–NCNT exhibited highest ORR onset potential of 0.88 V versus reversible hydrogen electrode and a current density of 3.7 mA cm−2 at 170 μg cm−2 of catalyst loading. The stability of the acid-treated Ni–TiO2–NCNT is proved by cyclic voltammetry and chronoamperometry measurements which are done for 800 cycles and 100 h, respectively. Primarily N doping of CNTs is the reason behind the improved ORR activity.

1. INTRODUCTION

Replacement of noble metal and noble metal-based electrocatalysts for cathodic oxygen reduction reaction (ORR) for fuel cells and metal–air batteries has become a potential area for research in the past few years.1–2 Recently, a significant volume of research has been devoted to the development of inexpensive catalysts with good ORR activity and stability. Among all of the catalysts reported in the literature, transition-metal (Fe, Ni, Co, and Mn) coordinated nitrogen–carbon and metal-free heteroatom-doped (B, N, F, and S) carbon materials show good ORR activity.3–9 Among all of the carbonaceous materials, carbon nanotubes (CNTs) possess good mechanical and chemical stability, high surface-to-volume ratio, and good electrical conductivity.10–12 Nitrogen doping of CNTs induces positive charge density on the adjacent carbon atoms. These sites show enhanced chemisorption of oxygen on the nitrogen-doped CNT (NCNT) surface and thereby leading to enhanced ORR activity.12–14 Stevenson et al. reported improvement in the ORR activity on the carbon nanofiber in alkaline and neutral media because of enhanced adsorption of oxygen and decomposition of peroxide intermediates.15 For ORR, a catalyst support plays very important role in long-term operations (simulated by load cycling and acceleration cycling).16 Among all of the catalyst supports reported, TiO2 acts as a promising catalyst support material because of its voltage stability and chemical stability.17 It prevents the agglomeration of the catalyst particles and provides thermal and oxidative stability. Although the semiconducting nature of TiO2 limits its conductivity,18–20 the synergistic effect between TiO2 and NCNT provides good conductivity and good stability. In the past years, researchers explored developing catalysts without direct metal nitrogen coordination through encapsulated metal atoms in a carbon matrix.20 Deng et al. investigated iron particle-encapsulated CNT, which showed effectively good ORR activity. Density functional theory (DFT) calculation has been done in order to probe the origin of interaction between iron and carbon on the surface of CNTs.21 Hu et al. showed that encapsulated metal particles helped in creating active sites in the outer graphitic layers and enhanced ORR activity.20

In this work, the nickel-encapsulated surface-modified NCNT on TiO2 (Ni–TiO2–NCNT) has been reported for ORR. Here, Ni–TiO2 was used to directly grow Ni-encapsulated nitrogen-doped high-surface-area CNTs by thermal decomposition of acetylene in the presence of acetonitrile vapor. This material was subjected to acid treatment to etch surface Ni to obtain Ni-encapsulated TiO2–NCNT.
2. RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of the synthesized samples along with the standard stick patterns of Ni, anatase TiO₂, and rutile TiO₂ are shown in Figure 1. From the XRD pattern of Ni–TiO₂ synthesized at 400 °C, the formation of metallic nickel and anatase TiO₂ phase is inferred. Peaks at 44.37°, 51.59°, and 76.08° are due to (111), (200), and (220) planes of nickel (ICDD card no. #00-001-1258), and the rest of the peaks corresponds to anatase TiO₂ (ICDD card no. #01-084-1285). In the presence of acetylene and/or acetonitrile vapor at 700 °C, TiO₂ has changed from the pure anatase to rutile phase. Peaks at 27.7°, 36.3°, 41.5°, 44.5°, 54.8°, 63°, 66.1°, 69.7°, 70.22°, and 75.27° correspond to (110), (101), (111), (210), (211), (221), (301), (112), and (320) planes of rutile TiO₂ (ICDD card no. #01-008-1173), respectively. Peak at 26.3° corresponds to the (002) plane of multiwalled CNTs (MWCNTs), and the one at 25.98° is probably for the exfoliated graphitic phase. Even after acid leaching, the presence of nickel (in acid-treated Ni–TiO₂–CNT and acid-treated Ni–TiO₂–NCNT) indicates the possible encapsulation of nickel metal particles inside the tubes, as this site is nonaccessible for acid to etch.

From the field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) spectra of Ni–TiO₂ (Figure 2a,f), the presence of Ni and anatase TiO₂ phase is inferred. EDX spectra of Ni–TiO₂–CNT, acid-treated Ni–TiO₂–CNT, Ni–TiO₂–NCNT, and acid-treated Ni–TiO₂–NCNT are given in the Supporting Information of the paper (Figure S1). Table S1 compares only the wt % of Ni and Ti as the other elements N, C, and O cannot be quantitatively estimated by EDX because of their low cross-sectional area. However, the EDX spectrum qualitatively indicates their presence.

From the FESEM of the Ni–TiO₂–CNT, it can be found that Ni acted as a catalyst for growing CNTs by following the tip growth mechanism on the TiO₂ support. Ni–TiO₂ particles are found decorating around the CNT surface (inset, Figure 2b). After acid treatment, the CNT surface turns smooth because of the removal of surface Ni (Figure 2d). After nitrogen doping, there is a change in the tube structure which is mainly due to the defects caused by N incorporation. After acid treatment, some defect sites in the structure have been introduced because of the removal of some amorphous carbon and surface nickel. To confirm the successful nitrogen doping and to study the distribution of the elements over the specified region, elemental mapping analysis has been carried out for Ni–TiO₂–CNT, Ni–TiO₂–NCNT, and acid-treated Ni–TiO₂–NCNT (Figure 3). Elemental mapping of Ni–TiO₂–NCNT confirms the presence of C, N, O, Ti, and Ni well distributed over the specified region shown in FESEM (Figure 3a). It also confirms that nitrogen is successfully incorporated into the CNT. Similarly, elemental mapping of Ni–TiO₂–CNT confirms the presence of C, O, Ti, and Ni. Before acid treatment, heavy Ni dispersion is seen throughout the CNTs of Ni–TiO₂–CNT and Ni–TiO₂–NCNT (Figure 3b). After acid treatment, dispersion of Ni got reduced significantly as surface Ni is dissolved leaving behind only the encapsulated Ni (Figure 3c).

While comparing the transmission electron microscopy (TEM) micrograph of (Figure 4) the Ni–TiO₂–CNT with Ni–TiO₂–NCNT, the surface of both the materials seems to be less crystalline in comparison to MWCNT’s crystallinity. As observed by XRD, the surface could be made of exfoliated graphite. In addition, the presence of some of the amorphous carbon cannot be ruled out. For N-doped CNTs, acetonitrile acted as nitrogen as well as carbon source. Nickel encapsulated...
inside the CNTs can be clearly seen which corroborates well with the XRD study of the samples. After acid treatment, CNT and NCNT surface get smoother because of the removal of surface Ni followed by stacking of the surface carbon structure on the CNT. Thickness of the nanotubes’ wall increases after acid treatment which probably supports the stacking of carbon layer attached on the CNT surface as a result of surface tension exerted by water during drying. Diameter of the nanotubes changed from 30 to 50 nm after acid treatment as seen in the TEM images.

Further, X-ray photoelectron spectroscopy (XPS) was done in order to investigate the successful N doping while using acetonitrile as the nitrogen source (Figure 5). The survey spectrum of the Ni–TiO$_2$–NCNT indicates the presence of oxygen, nitrogen, and carbon in the sample. Deconvoluted high-resolution C 1s spectra (Figure 5a) show the presence of C—C (284.5 eV), C—N (286.1 eV), and C=O (288.8 eV) species. High-resolution deconvoluted N 1s spectra indicate the presence of N atoms with three different binding energies corresponding to graphitic (401.3 eV), pyridinic (398.4 eV), and pyrrolic (400.3 eV). Atomic wt % of different N’s present is listed in Table 1. There are several reports in the literature which confirms the enhancement of ORR activity in the presence of pyridinic and pyrrolic N content. It is to be noted that Ti 2p and Ni 2p signals are not seen for the Ni–TiO$_2$–NCNT probably because of screening of TiO$_2$ and Ni by the carbon layers. The survey spectrum of Ni–TiO$_2$–NCNT and acid-treated Ni–TiO$_2$–NCNT is given in Figure 5i. While comparing Figure 5i, it is clear that there is a prominent presence of O in the surface. C 1s spectra clearly showed the presence of the functional groups because of acid treatment. In contrast to Ni–TiO$_2$–NCNT, an acid-treated counterpart shows clear presence of Ti and Ni. However, the Ni signal was very noisy as it was encapsulated

Figure 3. (a) Elemental mapping of Ni–TiO$_2$–NCNT. (b) Elemental mapping of Ni–TiO$_2$–CNT. (c) Elemental mapping of acid-treated Ni–TiO$_2$–NCNT.
inside the MWCNTs. Deconvolution of N 1s spectra yielded 4 types (pyridinic, pyrollic, graphitic, and pyridinic-N-oxide) of N, and their atomic % is reported in Table 1. Formation of pyridinic-N-oxide observed at the cost of pyridinic N while acid treating the Ni–TiO$_2$–NCNT. During acid treatment, pyridine is oxidized to pyridine-N-oxide. If we start with pyridine-N-oxide, while applying negative potential during ORR, it will turn into pyridine, which in turn will be available for ORR again. Ti 2p spectra clearly show the presence of TiO$_2$, and no other Ti species such as titanium nitrides and carbides, are present (they are expected at much lower binding energies).

Figure 6 shows Fourier transform infrared (FT-IR) spectra recorded for all of the samples. The peak at around 3572.7

Table 1. Composition of Nitrogen Functionalities in Ni–TiO$_2$–NCNT before and after Acid Treatment as Measured by XPS

| Nitrogen present     | Atomic wt % | Binding energy (eV) |
|----------------------|-------------|---------------------|
| Ni–TiO$_2$–NCNT      | Pyridinic   | 49.5                | 398.4 |
|                      | Pyrollic    | 31.4                | 400.3 |
|                      | Graphitic   | 19.1                | 401.3 |
| Acid-treated Ni–TiO$_2$–NCNT | Pyridinic   | 12.33               | 398.4 |
|                      | Pyrollic    | 29.45               | 400.3 |
|                      | Graphitic   | 22.34               | 401.3 |
|                      | Pyridinic-N-oxide | 35.88            | 405.8 |

Figure 4. TEM micrographs of (a) Ni–TiO$_2$–CNT, (b) acid-treated Ni–TiO$_2$–CNT (the inset shows at high magnification), (c) Ni–TiO$_2$–NCNT, and (d) acid-treated Ni–TiO$_2$–NCNT (the inset shows at high magnification).

Figure 5. XPS spectra of (a) C 1s, (b) N 1s, and (c) O 1s of Ni–TiO$_2$–NCNT. (d) C 1s, (e) N 1s, (f) O 1s, (g) Ni 2p, and (h) Ti 2p of acid-treated Ni–TiO$_2$–NCNT, and (i) survey spectra of Ni–TiO$_2$–NCNT (black) and acid-treated Ni–TiO$_2$–NCNT (red).
Peaks at 1240.8, 1960.6, and 1761.6 cm\(^{-1}\) correspond to C-O, C=O stretching, and C-H bending, respectively. Peaks at 2029.7, 2153.3, and 2454.9 cm\(^{-1}\) occurred due to C=C, C=C, and C=Br stretch, respectively. C=Br stretch could have originated from cetyltrimethyl ammonium bromide (CTAB) used in the synthesis of Ni-TiO\(_2\). The peak at 1631.8 cm\(^{-1}\) corresponds to C=N stretch.

All of the Raman modes of TiO\(_2\) (\(E_g\) at 144, 197 and 639 cm\(^{-1}\)), \(B_{1g}\) at 399 cm\(^{-1}\), and \(A_{1g}\) at 599 cm\(^{-1}\) were observed in the Raman spectra of all of the four samples, as shown in Figure 7. Peaks at \(\sim 1350\) and \(\sim 1580\) cm\(^{-1}\) are corresponded to D and G bands of carbon materials, respectively.\(^{32}\) The \(I_D/I_G\) ratio of all of the samples is calculated (Table 2) based on the area under G and D peaks. For undoped samples, the \(I_D/I_G\) ratio is higher compared to the doped one probably because acetonitrile (N source) acted both as the nitrogen and carbon source. However, acid treatment enhanced the \(I_D/I_G\) ratio, as new surface defects were incorporated by etching out of nickel and addition of functional groups (−OH and −COOH) by oxidation of the MWCNT surface by HNO\(_3\). For undoped samples, splitting of G band into G and D′ bands is probably due to the interaction between extended phonon modes of the graphitic phase with localized vibrational modes of the impurity present.\(^{33}\) Splitting of G band into D′ and G bands of the graphitic layer can be attributed as the result of intravalley phonon interaction with interband electronic transitions in the presence of Raman-active \(E_g\) modes. In the case of N-doped samples, the absence of D′ band is observed, which can be explained as the phonon energy normalization due to the allowed electronic interband transition in the graphitic layers.\(^{34,35}\)

Thermogravimetric analysis (TGA) of Ni-TiO\(_2\)-CNT, acid-treated Ni-TiO\(_2\)-CNT, Ni-TiO\(_2\)-NCNT, and acid-treated Ni-TiO\(_2\)-NCNT recorded in air atmosphere has been shown in Figure 8. A weight loss of 60, 50, 65, and 70% has been noted from TGA of Ni-TiO\(_2\)-CNT, acid-treated Ni-TiO\(_2\)-CNT, Ni-TiO\(_2\)-NCNT, and acid-treated Ni-TiO\(_2\)-NCNT. Because of the nitrogen doping surface area of the CNTs increased by 2.27 times that of the undoped CNTs and the acid treatment resulted in further increase (3.05 times) of surface area which is probably due to roughening of the CNT surface and loss of surface Ni. Higher surface area is beneficial as this would enhance the ORR current density.

Figure 10 shows the cyclic voltammetry (CV) obtained for all of the catalysts in O\(_2\)-saturated 0.1 N KOH solution. Onset potentials obtained from the linear sweep voltammetry (LSV) for the ORR are 0.76 V (Ni-TiO\(_2\)-CNT), 0.78 V (acid-treated Ni-TiO\(_2\)-CNT), 0.84 V (Ni-TiO\(_2\)-NCNT), and 0.88 V (acid-treated Ni-TiO\(_2\)-NCNT) versus reversible hydrogen electrode (RHE). Among all of the catalysts, the acid-treated Ni-TiO\(_2\)-NCNT shows the best performance. After acid treatment, ORR activity improved due to the CNT

Table 2. \(I_D/I_G\) Ratio of All of the Samples

| sample                  | \(I_D/I_G\) |
|-------------------------|-------------|
| Ni-TiO\(_2\)-CNT        | 1.22        |
| acid-treated Ni-TiO\(_2\)-CNT | 1.25        |
| Ni-TiO\(_2\)-NCNT      | 1.01        |
| acid-treated Ni-TiO\(_2\)-NCNT | 1.05        |

Figure 6. FTIR of all of the synthesized samples: Ni-TiO\(_2\)-CNT (black curve), acid-treated Ni-TiO\(_2\)-CNT (blue curve), Ni-TiO\(_2\)-NCNT (red curve), and acid-treated Ni-TiO\(_2\)-NCNT (green curve).

Figure 7. Raman spectra of (a) Ni-TiO\(_2\)-CNT, (b) acid-treated Ni-TiO\(_2\)-CNT, (c) Ni-TiO\(_2\)-NCNT, and (d) acid-treated Ni-TiO\(_2\)-NCNT.

Figure 8. TGA curves of Ni-TiO\(_2\)-CNT, acid-treated Ni-TiO\(_2\)-CNT, Ni-TiO\(_2\)-NCNT, and acid-treated Ni-TiO\(_2\)-NCNT.
surface roughening and adsorption of oxygen due to the positive charge density variation on the CNT surface induced by N doping.\textsuperscript{13}

In order to investigate the ORR activity further, LSV was performed at different rotation per minutes (rpm) (200–1600) (Figure 11). With the increase in the rotation speed, the increase in current confirms the supply of oxygen from the solution to the electrode surface (diffusion of O\textsubscript{2} species). For the Ni–TiO\textsubscript{2}–CNT, limiting the current density at 1600 rpm is found to be 2.7 mA cm\textsuperscript{–2}. After acid treatment, oxygen adsorption and product desorption get improved because of the defect induced by leaching of Ni on the CNT surface; therefore, overpotential for ORR got reduced. On nitrogen doping, because of charge delocalization on the CNT surface, an increase in current density was observed with simultaneous increase in the ORR onset potential (0.84 V vs RHE). After acid treatment, further lowering in overpotential (nearly 100 mV positive to that of Ni–TiO\textsubscript{2}–CNT) coupled with enhanced current density (3.7 mA cm\textsuperscript{–2} at 1600 rpm) was observed because of the removal of surface nickel with
concomitant increase in surface area and stacking of carbon layers leading to better chemisorptions of oxygen. Table 3 lists the ORR activity of the related materials reported in the literature. The Koutecky−Levich (K−L) analysis was conducted in order to find out the number of electrons involved in ORR at potential range 0.6−0.8 V versus RHE following eq 1

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{Bo^{1/2}}$$  \hspace{1cm} (1)

$$B = 0.201nFA\text{CD}_{O2}^{2/3}D_{O}^{-1/6}$$  \hspace{1cm} (2)

where $i$ = measured current density (mA cm$^{-2}$), $i_k$ = kinetic current density (mA cm$^{-2}$), $n$ = number of electron transfer, $F$ = Faraday constant (96 485 C mol$^{-1}$), $C$ = concentration of dissolved oxygen (1.26 $\times$ 10$^{-6}$ mol cm$^{-3}$), $D_O$ = diffusion coefficient of O$_2$ (1.93 $\times$ 10$^{-5}$ cm$^2$s$^{-1}$), $\nu$ = kinematic viscosity of the electrolyte (1.09 $\times$ 10$^{-2}$ cm$^2$s$^{-1}$), $A$ = electrode area, and $\omega$ = rpm.$^{35,58}$

The slope of $i^1$ versus $\omega^{-1/2}$ plot (Figure 12) was found to be nearly parallel to the theoretical four-electron line, and the actual number of electrons transferred per molecule of O$_2$ was calculated to be 3.4, 2.58, 3.43, and 3.6 for Ni−TiO$_2$−CNT, acid-treated Ni−TiO$_2$−CNT, Ni−TiO$_2$−NCNT, and acid-treated Ni−TiO$_2$−NCNT, respectively. It is to be noted that for unwashed samples, the $n$ value is about 3.4, and for acid-treated Ni−TiO$_2$−CNT, the $n$ value dropped to 2.58, indicating that Ni that was present on the surface of the nanotube contributed significantly toward four-electron transfer.$^{39}$ For acid-treated Ni−TiO$_2$−NCNT, doped N centers coupled with higher surface area of the catalyst and encapsulated Ni nanoparticles together contribute to four-electron ORR and higher limiting current.

Figure 13 shows the rotating ring-disk electrode (RRDE) plots recorded at 1600 rpm. A ring potential of 1.23 V versus RHE was applied. From the ring and disk currents, number of electrons involved and % of HO$_2^-$ production were estimated from eqs 3 and 4.

$$n = \frac{4 \times |I_{disk}|}{|I_{disk}| + |I_{ring}|/CE}$$  \hspace{1cm} (3)

$\%$ HO$_2^-$ = $\frac{2 \times |I_{ring}|/CE}{|I_{disk}| + |I_{ring}|/CE} \times 100$  \hspace{1cm} (4)

Number of electrons obtained from RRDE analysis is found to be 3.4, 2.45, 3.3, and 3.6 for Ni−TiO$_2$−CNT, acid-treated Ni−TiO$_2$−CNT, Ni−TiO$_2$−NCNT, and acid-treated Ni−TiO$_2$−NCNT, respectively (Figure 14), which corroborated...
well with the earlier calculation from the K−L analysis. For the acid-treated Ni−TiO$_2$−NCNT, ∼22% of HO$_2^-$ production has been estimated and number of electrons involved is found to be ∼3.6 which is best among the four catalysts. Guo et al. studied some highly oriented pyrolitic graphite model catalysts with well-controlled doping of N-species. By comparing the N 1s XPS of their model catalysts before and after subjecting to ORR in 0.1 M H$_2$SO$_4$, the presence of pyridonic N was confirmed. This species is observed when C atom next to N atom in pyridinic site reacts with OH species during ORR, converting pyridinic site to pyridonic site. Their DFT study in combination with local scanning tunneling microscopy (STM−STS) confirmed C atom next to N to possess a localized density of states near the Fermi level. Hence, we believe that C atom next to N of pyridinic and pyridine-N-oxide to be the active site for ORR.

From the LSV recorded at 1600 rpm, mass transfer corrected Tafel plot has also obtained from eq 5.

Figure 12. K−L plots of (a) Ni−TiO$_2$−CNT, (b) acid-treated Ni−TiO$_2$−CNT, (c) Ni−TiO$_2$−NCNT, and (d) acid-treated Ni−TiO$_2$−NCNT.

Figure 13. RRDE plots of (a) Ni−TiO$_2$−CNT, (b) acid-treated Ni−TiO$_2$−CNT, (c) Ni−TiO$_2$−NCNT, and (d) acid-treated Ni−TiO$_2$−NCNT in O$_2$-saturated 0.1 N KOH solution (rotation speed = 1600 rpm, scan rate = 20 mV s$^{-1}$ and temperature = 25 °C).
where $i_i$ = measured current density, $i_k$ = kinetic current density, and $i_L$ = the limiting current density.

Tafel analysis was performed in order to find the rate-determining step. Pt exhibits a Tafel slope of $\sim 60$ mV dec$^{-1}$ in the lower overpotential region in the alkaline solution.\(^4\) In this study, the Tafel slope of $\sim 60$ mV dec$^{-1}$ (below 0.75 V vs RHE) was obtained for the acid-treated Ni–TiO$_2$–NCNT (Figure 15a). Taylor and Humffray reported the Tafel slope to be as 60 mV dec$^{-1}$ for carbon materials in the alkaline solution (pH > 10).\(^5\) At high overpotential, the Tafel slope changes to 120 mV dec$^{-1}$, suggesting a change in the ORR mechanism from Temkin-type adsorption at lower potential to Langmuir adsorption at high potential.\(^4\)\(^2\)

In order to check the stability of the catalyst, 800 CV cycles were performed. Figure 15b compares the 1st and 800th cycles, which shows that the catalyst is highly stable even after 800 cycles. LSV at 1600 rpm has been recorded initially and after 800 cycles in order to further investigate the change in current density and onset potential. Current density after 800 cycles reduced by 200 mA cm$^{-2}$ but onset and half wave potential remained constant even after 800 cycles of operation at 1600 rpm (Figure 15c). Chronoamperometry study has been done for the best catalyst at 0 rpm in order to see the stability of the catalyst for 100 h at 0.6 V versus RHE, and from Figure 15d, it can be seen that the current has not changed much (in fact there is a slight increase in current with time) even after 100 h.

3. CONCLUSIONS

Among the four catalysts studied, the acid-treated Ni–TiO$_2$–NCNT showed the highest BET surface area of 206.47 m$^2$/g (3.05 times higher that of the Ni–TiO$_2$–CNT) as well as highest ORR activity in O$_2$-saturated 0.1 N KOH solutions. Although metal nanoparticles are present inside the CNTs–NCNTs, there seems to be no metal–nitrogen bonding at the surface of the CNTs–NCNTs. ORR onset potentials obtained from the LSV are 0.76 V (Ni–TiO$_2$–CNT), 0.78 V (acid-treated Ni–TiO$_2$–CNT), 0.84 V (Ni–TiO$_2$–NCNT), and 0.88 V (acid-treated Ni–TiO$_2$–NCNT) versus RHE. Among these, highest limiting current density ($i_L = 3.7$ mA cm$^{-2}$) is

\[
i_k = \frac{(i_i' - i)}{(i_i - i)}
\]

\[(5)\]
obtained for the acid-treated Ni−TiO2−NCNT and the \( n \) value calculated both from K−L and RRDE analyses is \( \sim 3.6 \) per oxygen molecule. In order to demonstrate the stability of the catalysts, 800 CV cycles were performed in \( \text{O}_2 \)-saturated 0.1 N KOH solutions. The 1st and 800th CV cycles showed nearly same activity. Chronoamperometry performed at 0.6 V versus RHE showed stable ORR performance for 100 h.

### 4. EXPERIMENTAL DETAILS

#### 4.1. Chemicals Used
Nickel nitrate hexahydrate (Ni\((\text{NO}_3)\)\(_2\)-6\(\text{H}_2\text{O}\)), titanium isopropoxide (Ti(OC\(_3\)H\(_7\))\(_4\)), isopropyl alcohol (IPA), CTAB, and potassium hydroxide (KOH) were purchased from Merck. All chemicals were used as received without further purification.

#### 4.2. Synthesis Process
To synthesize TiO\(_2\)-supported nickel, 5.85 g of Ni(NO\(_3\))\(_2\)-6\(\text{H}_2\text{O}\), 25 mL of Ti(OC\(_3\)H\(_7\))\(_4\), and 0.7 g of CTAB were added in 50 mL of IPA. Then, the mixture was charged into a 100 mL autoclave and subjected to the solvothermal process at 120 °C for 4.5 h in a tubular furnace. Thus, the obtained material (Ni−TiO\(_2\)) was used for growing CNTs through thermal decomposition of acetylene gas over the catalyst at 700 °C for 20 min in the presence of argon as a carrier gas. Argon flow (0.16 L/min) was maintained constant throughout the reaction, and hydrogen flow was maintained at 0.05 L/min during 500–700 °C. In order to obtain nitrogen-doped CNTs, acetylene gas was passed through the gas bubbler filled with acetonitrile solution preheated to 150 °C. As-synthesized samples were refluxed in concentrated nitric acid for 24 h to remove Ni from the surface (Scheme 1).

#### 4.3. Physical Characterization
Powder XRD patterns were recorded using a Bruker D8 ADVANCE X-ray diffractometer fitted with Cu K\(\alpha\) radiation (\( \lambda = 1.54 \) Å). All measurements were recorded in the 2\(\theta \) range of 20–80°. Vibrational spectral properties of samples were investigated using a PerkinElmer FT-IR spectrometer in the range 600–4000 cm\(^{-1}\). Raman spectra were recorded using a Bruker RFS 27 FT-Raman spectrometer in the range 50–2000 cm\(^{-1}\) (laser source wavelength = 632 nm). The SEM images and the energy-dispersive X-ray spectra (EDAX) were taken employing an Inspect F scanning electron microscope. TEM images were taken in a Philips CM 12 instrument. TGA was carried out using SDTQ600 from TA Instruments in air atmosphere from room temperature to 1000 °C at 20 °C min\(^{-1}\) heating rate. XPS measurements were recorded using an Omicron ESCA Probe spectrometer fitted with polychromatic Mg K\(\alpha\) X-rays (\( \hbar \nu = 1253.6 \) eV) operated at ultrahigh vacuum (10\(^{-9}\) mbar). X-ray power applied was 300 W.

#### 4.4. Electrochemical Characterization
The catalyst sample (3 mg) was dispersed in 1.5 mL of IPA–water solution (1:2 V/V) in an ultrasonic bath to obtain a homogeneous ink. The Nafion ionomer solution (5 μL; 5 wt %) was then added as a binder. The catalyst ink was coated on the glassy carbon electrode. Catalyst loading on the glassy carbon electrode is 170 μg cm\(^{-2}\). Catalyst loading reported in the literature is varied from 80 to 300 μg cm\(^{-2}\).

#### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01565.

Additional information including EDX spectra (PDF)

#### AUTHOR INFORMATION

**Corresponding Authors**

*E-mail: ramp@iitm.ac.in (R.S.).
*E-mail: rkraman@iitm.ac.in (K.R.).

**ORCID**

Ramprabhu Sundara: 0000-0002-7960-9470
Kothandaraman Ramanujam: 0000-0003-2231-2665

**Notes**

The authors declare no competing financial interest.

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