In the current work, we reported the \textit{in situ} fabrication of a nickel vanadate (Ni$_3$V$_2$O$_8$)-anchored N-doped reduced graphene oxide (NRGO) hybrid by a simple one-step reflux method. Subsequently, the electrocatalytic performance of the Ni$_3$V$_2$O$_8$/NRGO hybrid was investigated in an alkaline medium (1.0 M KOH) for the hydrogen evolution reaction (HER). It was noted that the optimization of the NRGO content (5.6 wt%) highly influenced the homogeneous distribution of quasi-spherical Ni$_3$V$_2$O$_8$ nanoparticles over NRGO sheets and enhanced the water reduction ability. This hybrid material exhibited a sufficiently high electrochemical active surface area (517.5 cm$^2$) and remarkably low charge transfer resistance (~1.6 Ω). Furthermore, the very low overpotential (~43 mV) and the high exchange current density (~1.24 mA cm$^{-2}$) of Ni$_3$V$_2$O$_8$/NRGO (5.6 wt%) demonstrated its promising HER performance. Additionally, superior long-term and accelerated stability compared to that of the benchmark Pt/C in a strong basic medium clearly signified that Ni$_3$V$_2$O$_8$/NRGO (5.6 wt%) can act as an efficient, cost-effective, and durable electrocatalyst for water electrolyzers.

Hydrogen is one of the most important alternative fuels compared to many conventional energy resources. In this regard, the electrolysis of water in an alkaline medium remains the most cost-effective, sustainable and industrially accepted method for hydrogen production. However, the high overpotential of the hydrogen evolution reaction (HER) affects the efficiency of hydrogen generation. Therefore, it is mandatory to lower the overpotential of HER in the presence of suitable electrocatalyst(s). As a result, platinum (Pt) has been reported to be the most active HER electrocatalyst of recent times. However, the widespread use of Pt for industrialization and commercialization is limited due to its scarcity, very high cost and inferior durability in strong alkaline solutions. According to the available literature, mixed transition metal oxides compared to the corresponding monometallic oxides show better electrochemical activity due to the presence of a large number of active sites. In this regard, transition metal vanadates, especially Ni$_3$V$_2$O$_8$, Co$_3$V$_2$O$_8$, and CoVO$_x$, exhibit enhanced electrochemical activity owing to the multiple valence oxidation states of vanadium. In view of this, Ni$_3$V$_2$O$_8$ nanowires grown on a Ti-foil, Ni$_3$V$_2$O$_8$/carbon cloth, urchin-shaped Ni$_3$(VO$_4$)$_2$ hollow nanospheres, nickel vanadate nanocages, and Ni$_3$(VO$_4$)$_2$/rGO nanocomposites have been successfully investigated for their applications in lithium-ion batteries, sodium-ion batteries, and supercapacitors. However, there exists very limited literature related to the application of Ni$_3$V$_2$O$_8$ in electrocatalytic energy conversions. Shang et al. observed a moderate overpotential of ~113 mV at 10 mA cm$^{-2}$ current density for HER in a 1.0 M KOH solution in the nickel foam-supported combination of two mixed transition metal oxides (Ni$_3$(VO$_4$)$_2$@NiCo$_2$O$_4$/NF). In addition, sea-urchin-like Ni$_3$(VO$_4$)$_2$ nanostructures showed promising electrocatalytic HER activity with a very small overpotential (910) of about 90 mV at 10 mA cm$^{-2}$ and a small Tafel slope (50 mV dec$^{-1}$) in 0.5 M H$_2$SO$_4$. However, the low charge transfer resistance and stability of electrocatalysts (non-precious) in a strong alkaline medium are few other desirable parameters to be taken into consideration for their superior electrocatalytic performance. Motivated by these facts, we focused our work on the fabrication of a nickel vanadate (Ni$_3$V$_2$O$_8$) nanoparticle-decorated nitrogen-doped RGO (NRGO) hybrid through a simple one-step reflux method (ESI†). Scheme 1 clearly demonstrates the \textit{in situ} fabrication of the Ni$_3$V$_2$O$_8$/NRGO hybrids. The choice of NRGO in the present work was mainly guided by its high electrical conductivity and the presence of larger defects. Therefore, it is anticipated that the structural stability of the electrode material can be enhanced in the presence of NRGO as the conducting backbone in a strong alkaline medium. Notably, to...
the best of our knowledge, no reports are available on evaluating the electrocatalytic HER performance of an Ni$_3$V$_2$O$_8$/NRGO hybrid in an alkaline solution. In this context, our findings showed that the Ni$_3$V$_2$O$_8$/NRGO (~5.6 wt%) hybrid demonstrated superior HER activity in an alkaline medium.

The formation pathway of the Ni$_3$V$_2$O$_8$/NRGO hybrids through a simple one-step reflux method, as displayed in Scheme 1, consists of the adsorption of Ni$^{2+}$ ions on the surface of graphene oxide (GO). This is most likely due to the electrostatic attraction between the positively charged metal ions (Ni$^{2+}$) and the negatively charged oxygen functionalities (–COOH, –OH) of GO (Fig. S2†). Subsequently, the solutions of NH$_4$VO$_3$ (2 mmol) and urea (12 mmol) prepared in a mixed solvent (water + EG) were added to the earlier dispersion of Ni$^{2+}$/GO. As a result, NH$_3$ (source of nitrogen) was formed during the hydrolysis and the transesterification of urea in the presence of water and ethylene glycol, respectively. In addition, Ni$^{2+}$ and VO$_3^-$ ions originating from NiCl$_2$·6H$_2$O and NH$_4$VO$_3$ combined together to form Ni$_3$V$_2$O$_8$ in the basic medium. Furthermore, ammonia generated during the hydrolysis and the transesterification of urea successfully reduced GO to RGO, followed by simultaneous N doping to form the Ni$_3$V$_2$O$_8$/NRGO hybrid. The plausible reactions involved in the fabrication of the Ni$_3$V$_2$O$_8$/NRGO hybrid can be summarized as follows:\(^\text{(1)}\)

\[
\text{Ni}^{2+} + \text{GO} \rightarrow \text{Ni}^{2+}/\text{GO} \\
\text{CO(NH$_3$)$_2$} + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2 \\
\text{CO(NH$_3$)$_2$} + \text{HO–CH$_2$CH$_2$–OH} \rightarrow (\text{CH$_2$O})_2\text{CO} + 2\text{NH}_3 \\
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \\
3\text{Ni}^{2+}/\text{GO} + 2\text{VO}_3^- + 4\text{OH}^- \rightarrow \text{Ni}_3\text{V}_2\text{O}_8/\text{NRGO} + 2\text{H}_2\text{O} \\
\]

(5)

Thermogravimetric analysis (TGA) in air revealed that the NV/NRGO1, NV/NRGO2, and NV/NRGO3 hybrids contained ~3.3, 5.6, and 6.6 wt% NRGO, respectively (ESI†). Furthermore, the results of the CHN analyses of the hybrids were also in agreement with the TGA results (Table S1†). The X-ray diffraction (XRD) patterns of the NV, NRGO, and NV/NRGO hybrids were obtained and the corresponding findings are displayed in Fig. 1a. The XRD pattern of NRGO showed the appearance of peaks at ~23.8° (002) and ~43.0° (100) similar to that reported for reduced graphene oxide.\(^\text{23}\) It is also evident from Fig. 1a that the XRD patterns of NV as well as NV/NRGO hybrids show the formation of the pure orthorhombic phase (JCPDS no. 74-1484) of Ni$_3$V$_2$O$_8$ without any impurity peaks corresponding to NiO or V$_2$O$_5$. Interestingly, the intensity of the NRGO peaks almost disappeared for NV/NRGO hybrids, indicating the possible formation of Ni$_3$V$_2$O$_8$ on highly exfoliated NRGO sheets. This could be further ascertained by the morphological investigations of the NV/NRGO hybrids through electron microscopy. The Raman spectra (Fig. 1b) show that the peaks appearing at 760 cm$^{-1}$ (low intensity) and 823 cm$^{-1}$ (high intensity) for NV correspond to the asymmetric and symmetric stretching vibration modes of the V=O bonds.\(^\text{33,34}\) However, the intensity of the peak at 823 cm$^{-1}$ is considerably reduced for all the hybrids, while the peak corresponding to ~760 cm$^{-1}$ almost disappears for the NV/NRGO3 hybrids compared to that for NV. The Raman spectra of the NV/NRGO hybrids also exhibit the presence of D (~1596 cm$^{-1}$) and G (~1359 cm$^{-1}$) bands appearing at nearly identical positions. This finding suggests that the graphitic structure remains unaltered in the hybrids.\(^\text{33}\) Furthermore, the $I_D/I_G$ ratios corresponding to the NV/NRGO hybrids were calculated and followed the order NV/NRGO2 (0.86) > NV/NRGO1 (0.84) > NV/NRGO3 (0.76). The relatively higher value of the $I_D/I_G$ ratio in NV/NRGO2 could be ascribed to the presence of higher defects/disorders.\(^\text{34}\)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{XRD patterns (a) and Raman spectra (b) of NRGO, NV, NV/NRGO1, NV/NRGO2, and NV/NRGO3.}
\end{figure}

The Raman photoelectron spectroscopy (XPS) survey scans of NV and NV/NRGO2 are displayed in Fig. 2a. Furthermore, the high-resolution Ni 2p and V 2p spectra of NV were compared with that of NV/NRGO2 (Fig. S4†). It was noted that the Ni 2p and V 2p peaks present in NV/NRGO2 shifted to higher binding energies with respect to that for NV due to the strong electronic interaction between Ni$_3$V$_2$O$_8$ and NRGO present in NV/NRGO2. Such interaction between C/N (NRGO) and Ni/V (Ni$_3$V$_2$O$_8$) that leads to an increase in the respective binding energies can be accounted on the basis of the reduction in the electron density around Ni/V in NV/NRGO2 as a result of their electronegativity ($\chi$) differences ($\chi_{\text{Ni}} = 1.91$, $\chi_{\text{V}} = 1.63$, $\chi_{\text{C}} = 2.55$, $\chi_{\text{N}} = 3.04$).\(^\text{25}\)

The survey spectrum (Fig. 2a) of NV/NRGO2 clearly shows the
presence of Ni, V, O, C, and N. Fig. 2b–f show the high-resolution core levels and the corresponding deconvoluted spectra of Ni 2p, O 1s, V 2p, C 1s, and N 1s, respectively. The peaks at 873.0 eV (Ni 2p\textsubscript{1/2}) and 855.4 eV (Ni 2p\textsubscript{3/2}) in Ni 2p spectra correspond to the presence of Ni\textsuperscript{2+} in NV/NRGO\textsubscript{2}.\textsuperscript{16,17} This is also supplemented by the presence of satellite peaks at 881.2 and 861.6 eV.\textsuperscript{16} In addition, the peaks at 875.1 eV (Ni 2p\textsubscript{1/2}) and 857.1 eV (Ni 2p\textsubscript{3/2}) can be assigned to the existence of Ni\textsuperscript{3+}.

In the case of O 1s, the peaks at ~530.1, 531.6, and 533.0 eV correspond to the metal–oxygen bond, oxygen vacancies, and surface –OH groups.\textsuperscript{15} Furthermore, the peaks at ~524.0, 518.5, and 516.7 eV in the V 2p spectrum can be attributed to the +5 oxidation state of V.\textsuperscript{17} The intense peak at 284.4 eV in the C 1s spectrum corresponds to sp\textsuperscript{2} hybridized graphitic C originating from NRGO.\textsuperscript{4} The other additional peaks at ~290.7, 288.1, and 285.3 eV can be assigned to C=O, N–sp\textsuperscript{3}C, and N–sp\textsuperscript{3}C, respectively.\textsuperscript{15} The peaks in the spectrum of N 1s can be indexed to graphitic-N (401.3 eV), pyrrolic-N (399.6 eV), and pyridinic-N (398.3 eV).\textsuperscript{4} These findings clearly demonstrate the nitrogen doping (~1.6 at%) of RGO and the formation of highly pure Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8}/NRGO hybrids. Also, the presence of pyrrolic-N is responsible for the high electrical conductivity of NRGO, while pyridinic-N facilitates electrocatalytic activity.\textsuperscript{28} Therefore, the optimised NRGO content in NV/NRGO\textsubscript{2} is most likely to enhance the electrocatalytic HER performance of Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8}.

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were employed to reveal the formation of the aggregated sub-micrometre hierarchical spherical particles of NV (Fig. 3a and e) and the distribution of Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8} particles on NRGO sheets for the NV/NRGO hybrids (Fig. 3b–h). It was clearly seen that the addition of NRGO resulted in a narrow size and better distribution of the Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8} particles on the NRGO sheets compared to that for pure NV. Furthermore, a lower degree of exfoliation of NRGO in the NV/NRGO\textsubscript{1} hybrid was observed (Fig. 3b and f). It was noted that the agglomerated Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8} particles covered entire NRGO sheets and bare sheets of NRGO were hardly visible. When the amount of GO was increased during the preparation of the NV/NRGO\textsubscript{2} hybrid, relatively better exfoliation of NRGO and uniform distribution of Ni\textsubscript{3}V\textsubscript{2}O\textsubscript{8} particles were observed over the NRGO sheets, as displayed in Fig. 3c and g. The FESEM/TEM images of the NV/NRGO\textsubscript{3} hybrid in Fig. 3d and h indicate the irregular distribution of NV particles on NRGO sheets due to their self-agglomeration with the visible bare surface of NRGO, indicating its incomplete coverage. Considering all these observations, it is anticipated that the optimization of the GO/
Ni$_3$V$_2$O$_8$ ratio in the fabrication of the NV/NRGO hybrids is the key factor to achieve uniform distribution of the NV particles on the NRGO sheets. Furthermore, the high-magnification FESEM and TEM images (Fig. S5a and b†) of the NV/NRGO2 hybrid also reaffirmed our earlier contention on the homogeneous distribution of the Ni$_3$V$_2$O$_8$ nanoparticles on the NRGO sheets. The corresponding HRTEM image of the NV/NRGO2 hybrid is also displayed in Fig. S5c†. It clearly indicates the growth of the (122) plane ($d = 0.249$ nm), and the presence of concentric rings in the selected area diffraction pattern (SAED) (in the inset of Fig. S5c†) demonstrates its polycrystalline nature. The elemental composition analysis of the marked region of NV/NRGO2 in Fig. S5d† was carried out through STEM-elemental mapping and the results are displayed in Fig. S5(e–h),† which clearly demonstrate the presence of Ni, V, O, and N in NV/NRGO2. It may be noted that the mapping of C was not taken into account due to its presence in the carbon-coated copper grid. The energy dispersive X-ray (EDX) analysis of NV/NRGO2 in Fig. S6† also confirms that the Ni-to-V atomic ratio is $\sim$3 : 2, indicating the formation of Ni$_3$V$_2$O$_8$, as observed from the XRD analysis (Fig. 1a). In addition, the Ni-to-V molar ratio ($\sim$1.59) obtained from the ICP-MS analysis (Table S2†) confirmed our observations obtained from EDX.

The electrocatalytic HER polarization curves of Pt/C (20 wt%) and the NV, NRGO, NV/RGO and NV/NRGO hybrids (scan rate: 5 mV s$^{-1}$) in 1.0 M KOH are displayed in Fig. 4a. The overpotentials ($\eta$) required to achieve 10 mA cm$^{-2}$ cathodic current density were found to be $\sim$16, 97, 194, 236, 94, 43, and 81 mV for Pt/C, NV, NRGO, NV/RGO, NV/NRGO1, NV/NRGO2, and NV/NRGO3, respectively. Our investigations on the HER activity of NV ($\eta_{10} = 97$ mV) and NRGO sheets ($\eta_{10} = 194$ mV) established the synergistic effect in NV/NRGO2 ($\eta_{10} = 43$ mV). Furthermore, control experiments were also performed on NiO and V$_2$O$_5$ to evaluate their performance in HER (Fig. S7†). It was observed that NiO ($\eta_{10} = 200$ mV) and V$_2$O$_5$ ($\eta_{10} = 163$ mV) individually exhibit lower activities compared to NV ($\eta_{10} = 97$ mV) in HER. Therefore, the synergistic contribution of NiO and V$_2$O$_5$ in addition to that of NV and NRGO as stated earlier can account for the improved hydrogen evolution ability owing to the synergistic effect in NV/NRGO2. It was noted that NV/NRGO1 showed a slightly better performance compared to NV in the low overpotential region although its performance deteriorated at higher overpotentials (Table S3†). This phenomenon could be attributed to the low exfoliation of NV/NRGO as well as the aggregation and surface blockage of the Ni$_3$V$_2$O$_8$ particles in NV/NRGO1. Alternatively, the possibility of a less number of active sites coming in contact with the electrolyte as a result of the faster rate of hydrogen evolution at the high overpotential regions could not be overruled. In contrast, NV/NRGO2 loaded with 5.6 wt% of NRGO achieved the lowest value of $\eta_{10}$ (43 mV), demonstrating its superior electrocatalytic HER activity. Such superior HER activity of NV/NRGO2 could be assigned to the uniform distribution of quasi-spherical Ni$_3$V$_2$O$_8$ nanoparticles on NRGO sheets, thereby facilitating a better contact between active sites and the electrolyte (OH$^{-}$ ions). However, the NV/NRGO3 (6.6 wt%) hybrid exhibited lower electrocatalytic activity due to the restacking of NRGO sheets, self-agglomeration, and the irregular distribution of catalytic active sites. Scheme 2 shows the distribution of the active sites in NV/NRGO1, NV/NRGO2, and NV/NRGO3 considering these aspects and the TEM studies discussed earlier. Furthermore, the HER performance of NV/RGO was also compared with that of the NV/NRGO2 hybrid to ascertain the advantages of NRGO if any. Our findings clearly demonstrated the relative inferior performance of NV/RGO ($\eta_{10} = 236$ mV) due to the poor exfoliation/aggregation of RGO sheets and NV particles, as evident from the FESEM image (Fig. S8b†). In contrast, NV/NRGO2 displayed a superior HER performance due to the homogeneous distribution of NV particles in the NRGO matrix, as indicated by the TEM image shown in Fig. S5b.† Alternatively, the fact that the presence of enhanced defect sites in NRGO can contribute to the improvement in its HER activity also cannot be ruled out. According to our findings, NV/NRGO2 also outperformed other HER electrocatalysts such as Ni$_3$(VO$_4$)$_2$@NiCo$_2$O$_4$/NF (113 mV),$^{18}$ Ni$_3$N@VN-NF (56 mV),$^{19}$ N–Co–C/RGO (130 mV),$^{20}$ Sr$_2$RuO$_4$ (61 mV),$^{21}$ β-Ni(OH)$_2$/Pt (108 mV),$^{22}$ and nest-like NiCoP (62 mV)$^{14}$ (Table S4†).

A Tafel slope is useful to gain insights into the mechanistic pathway through the rate-determining step (RDS). According to
the available literature, HER in an alkaline medium proceeds through the Volmer–Heyrovsky or Volmer–Tafel pathways. In the Volmer step, the dissociation of a surface-adsorbed water molecule results in the formation of surface-adsorbed hydrogen atoms (S–H\textsubscript{ad}) and the generation of OH\textsuperscript{−} (H\textsubscript{2}O + S + e\textsuperscript{−} → S–H\textsubscript{ad} + OH\textsuperscript{−}). Subsequently, S–H\textsubscript{ad} either combines with another H\textsubscript{2}O molecule in the Heyrovsky step (H\textsubscript{2}O + S–H\textsubscript{ad} + e\textsuperscript{−} → H\textsubscript{2} + S + OH\textsuperscript{−}) or recombines with another S–H\textsubscript{ad} to release molecular hydrogen in the Tafel step (2S–H\textsubscript{ad} → 2S + H\textsubscript{2}). According to the Butler–Volmer kinetics, the rate-determining step can be identified depending on the Tafel slope as the Volmer (120 mV dec\textsuperscript{−1}), Heyrovsky (40 mV dec\textsuperscript{−1}), or Tafel (30 mV dec\textsuperscript{−1}) reaction. We observed the Tafel slope (Fig. 4b) values of ~30.3, 57.8, 65.6, 94.3, 81.4, 54.8, and 83.8 mV dec\textsuperscript{−1} corresponding to Pt/C, NV, NRGO, NV/RGO, NV/NRGO1, NV/NRGO2, and NV/NRGO3. These findings suggested Volmer and Heyrovsky reactions as the rate determining steps, confirming the overall Volmer–Tafel and Volmer–Heyrovsky pathways in Pt/C and NV/NRGO2 (Scheme 3), respectively. It was anticipated that the relatively lowest Tafel slope of NV/NRGO2 (54.8 mV dec\textsuperscript{−1}) among those of NV and all its NRGO hybrids, would indicate faster reaction kinetics in HER. It was also noted that the Tafel slope for NV/NRGO2 (54.8 mV dec\textsuperscript{−1}) was lower in comparison to the results of the electrocatalysts studied in the contemporary works reported in the literature such as NiO/Ni-CNT (84.6 mV dec\textsuperscript{−1}),\textsuperscript{17} VOOH hollow nanospheres (104 mV dec\textsuperscript{−1}),\textsuperscript{18} Fe\textsubscript{17.5%}–Ni\textsubscript{8.5%}S\textsubscript{2}/NF (95 mV dec\textsuperscript{−1}),\textsuperscript{19} P\textsubscript{8.5%}–Co\textsubscript{1.5%}O\textsubscript{1.5%}/NF (86 mV dec\textsuperscript{−1}),\textsuperscript{20} Cu NDS/Ni\textsubscript{3}S\textsubscript{2} NTs-CFs (76.2 mV dec\textsuperscript{−1}),\textsuperscript{33} and Ni\textsubscript{3}N@CQDs (108 mV dec\textsuperscript{−1})\textsuperscript{40} for HER in an alkaline medium.

Moreover, exchange current density (j\textsubscript{0}) is an important parameter to assess the intrinsic electrocatalytic activity of a catalyst. In this regard, the Tafel plot was extrapolated to η = 0 and the j\textsubscript{0} values of NV (0.05 mA cm\textsuperscript{−2}), NV/NRGO1 (0.86 mA cm\textsuperscript{−2}), NV/NRGO2 (1.24 mA cm\textsuperscript{−2}) and NV/NRGO3 (1.04 mA cm\textsuperscript{−2}) were evaluated, as shown in Fig. 4c. The excellent HER activity of NV/NRGO2 is reflected from its j\textsubscript{0} value, which is closer to that of Pt/C (1.62 mA cm\textsuperscript{−2}). Furthermore, the intrinsic activity of an electrocatalyst can be correlated to the turnover frequency (TOF). Accordingly, the TOF values at η = 100 mV follow the order NV/NRGO2 (0.021 s\textsuperscript{−1}) > NV/NRGO1 (0.013 s\textsuperscript{−1}) > NV/NRGO3 (0.008 s\textsuperscript{−1}) > NV/NRGO2 (0.004 s\textsuperscript{−1}). The highest TOF value of NV/NRGO2 further confirmed our earlier contention on its superior intrinsic HER activity. The electrochemical active surface area (ECSA) is an important parameter for the surface redox reactions at the electrode.\textsuperscript{44} Accordingly, the obtained ECSA values (ESI†) follow the order (Fig. S11b†) NV (92.5 cm\textsuperscript{2}) > NV/NRGO1 (297.5 cm\textsuperscript{2}) > NV/NRGO3 (455.0 cm\textsuperscript{2}) > NV/NRGO2 (517.5 cm\textsuperscript{2}). These findings clearly suggest that NV/NRGO2 consists of a large number of active sites owing to its highest ECSA compared to all other synthesized electrocatalysts. The Nyquist plots (η = 244 mV) of NV, NRGO, NV/RGO, NV/NRGO1, NV/NRGO2, and NV/NRGO3 in Fig. 4d demonstrate the corresponding Rs\textsubscript{ct} values of ~57.1, 2.2, 15.4, 12.6, 1.6, and 6.9 Ω. The high electronic conductivity of the NRGO sheets accounted for the significantly decreased Rs\textsubscript{ct} value for the NV/NRGO hybrids in comparison to that for NV. Furthermore, the remarkably low Rs\textsubscript{ct} value (1.6 Ω) of NV/NRGO2 also supported its highly enhanced HER activity.

The long-term stability and the durability of an electrocatalyst are considered to be the most important criteria for its practical applications.

\textsuperscript{35,40} In view of this, Pt/C and NV/NRGO2 were investigated by the chronopotentiometry (CP) technique (without iR-compensation) at 10 mA cm\textsuperscript{−2} for their long-term durability (12 h); potential (E) versus time (t) is displayed in Fig. 4e. Our findings demonstrated the appearance of three regions in the E vs. t plot of NV/NRGO2: 92 mV (t = 0) to 149 mV
ruled out. An additional low intense peak also appeared at 11.3 
used in the preparation of the working electrode also cannot be 
tively, the possibility of a peak appearing due to carbon black 
ascribed to the presence of graphitic carbon in NRGO. Alterna-
A similar behaviour was also noticed for NiCo2S4/NF 
addition, the appearance of the (002) peak at 23.1 
alkaline medium.

Fig. S13(i).

patterns of NVNRGO2 before and a 

NVNRGO2 a 

the orthorhombic phase of Ni3V2O8 (JCPDS no. 74-1484). In 

was studied by XRD, FESEM and Raman spectroscopy; the cor-
responding findings are displayed in Fig. S13.† The XRD 
patterns of NVNRGO2 before and after HER are compared in 

† The appearance of prominent peaks at 35.1° (122), 43.0° (151), and 62.5° (004) is noted in the XRD pattern of 

NVNRGO2 after electrocatalysis (Fig. S13(ib)†), corresponding to the 

orthorhombic phase of Ni3V2O8 (JCPDS no. 74-1484). In 

addition, the appearance of the (002) peak at 23.1° can be 

ascribed to the presence of graphitic carbon in NRGO. Alterna-

ly, the possibility of a peak appearing due to carbon black 

used in the preparation of the working electrode also cannot be 

ruled out. An additional low intense peak also appeared at 11.3°, 

which could be assigned to the (003) plane of NiOOH (JCPDS no. 

06-0075) due to the continuous electrolysis of NV/NRGO2 in the 

alkaline medium.† Furthermore, the Raman spectrum of the 

sample (after HER) remains more or less unaltered except for the 

slightly reduced Ip/Io ratio (0.82) with respect to that for pristine 

NV/NRGO2. This could be attributed to the decrease in the 

density of the defects in NV/NRGO2 after the HER durability test. 
The XPS analysis of NV/NRGO2 was also performed after the 

stability test and the corresponding findings are displayed in 

Fig. S14.† The XPS survey scan of the post-HER sample 
demonstrated the presence of Ni, V, O, C, and N similar to that 

for the fresh catalyst. The high-resolution Ni 2p spectrum of the 

sample after the stability test shows negligible shifts in Ni 2p1/2 

(872.9 eV) and Ni 2p3/2 (855.0 eV) peaks compared to the 

spectrum of the sample before HER. In contrast, two additional 

peaks appear at 873.5 and 856.2 eV in the deconvoluted 

spectrum of Ni 2p. This can be ascribed to the formation of NiOOH 

owing to the surface oxidation of the catalyst by adsorbed OH−

ions as a result of prolonged use in a strong alkaline medium.† Similarly, the new peaks observed in the V 2p region at 521.8 and 515.2 eV can be assigned to VOOH.† In addition, the O 1s spectrum shows peaks at 531.1, 530.2, and 528.6 eV due to H2O, O–H, and the metal–oxygen bond, respectively.‡ In addition, the comparison of the FESEM images of NV/NRGO2 before (Fig. 3c) and after (Fig. S13(ii)†) HER shows some changes in the morphology due to the presence of carbon black and the poly-

meric binder (PVDF) used in electrode preparation. All these 

findings further strengthen our earlier inference: NV/NRGO2 is a 
suitable electrocatalyst for practical applications.

The superior HER activity of NV/NRGO2 to those of other 
electrocatalysts may be ascribed to the synergistic effect of 

Ni3V2O8x particles with NRGO sheets, uniform particle 
distribution, N doping, and the optimised NRGO content. 

Alternatively, the remarkable increase in the charge trans-
portation of NRGO due to high electrical conductivity also 
cannot be ruled out. Furthermore, the higher ECSA value of 

NVNRGO2 (517.5 cm2) most likely originates from the better 
exposure of the electrolyte to the active sites. Additionally, 

NRGO also imparted structural stability in its long-term appli-
cation, as evidenced by post-HER characterizations. Therefore, 

NV/NRGO2 can act as an effective and stable electrocatalyst in 
an alkaline medium for the hydrogen evolution reaction.

Our findings clearly showed that NV/NRGO2 exhibited 
superior durability in contrast to other electrochemical pro-

cesses compared to commercial Pt/C. Most likely, Pt/C facilitates 

the exposure of relatively more active sites to enable rapid 
electron and mass transfer.† Similar HER activity could be 

achieved for NV/NRGO2 by generating more active sites viâ 
tuning its morphology or by the modification of the electronic 
structure by doping.† According to the available literature, an 
effective alkaline HER electrocatalyst should have the ability of 
efficient water dissociation at the surface and proper binding 

with hydrogen intermediates.† This could be facilitated by 

adding another active component on the surface of NV/NRGO2 
to achieve similar/better HER activity to/than that of Pt/C in an 

alkaline medium.‡−§

In summary, an Ni3V2O8/NRGO hybrid with 5.6 wt% NRGO 
content was successfully fabricated through refluxing 

and employed as an electrocatalyst for HER in an alkaline medium 

(1.0 M KOH). The superior performance of the Ni3V2O8/NRGO 
(5.6 wt%) hybrid manifested a very low overpotential (~43 mV), 

small Tafel slope (~54.8 mV dec−1), and quite high exchange 
current density (~1.24 mA cm−2) for hydrogen evolution in 

1.0 M KOH. Furthermore, the value of the Tafel slope suggested 

that HER proceeded through the Volmer–Heyrovsky mecha-
nism. In addition, this hybrid electrocatalyst also demonstrated 
good long-term and accelerated stability in a strong alkaline 
solution. Therefore, Ni3V2O8/NRGO (5.6 wt%) can be used as a 

low-cost, highly efficient, and stable alternative to the 

commercial Pt/C electrocatalyst for the industrial production of 

hydrogen through alkaline water electrolysis.

Conflicts of interest

There are no conflicts of interest to declare.
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