Electro-catalytic hydrogen evolution and magnetic behavior of N-doped-rGO supported Ni_xP_y

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Abstract

Search for cost effective, earth abundant electrocatalysts for hydrogen generation through water splitting is the challenge of the hour whereas multifunctional applicability of the materials is the extremely sought issue for multi-tasking smart materials. In this work, nitrogen doped reduced graphene oxide (N-rGO) supported nickel phosphide (Ni_xP_y) nanomaterial has been prepared and characterized. Details electrocatalytic measurements exhibit the commendable performance of the composite materials against hydrogen evolution reaction in acid medium. The reduction of the required overpotential for reaching 10 mA/cm^2 from 265 mV (Ni_xP_y) to 248 mV ($\text{Ni}_x\text{P}_y/\text{N-rGO}$) is observed in $0.5 \text{ M H}_2\text{SO}_4$ solution which proves the benefit for attaching N-rGO with Ni_xP_y . The electrochemical active surface area measurement also ascertains the quality of the composite and the enhancement of an active surface area is attributed to the attachment of N-rGO matrix. Furthermore, the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite confirms its stability in the acidic medium for 1200 min at 248 mV without any significant loss of current. Ground state ferromagnetic behavior has been demonstrated by $\text{Ni}_x\text{P}_y/\text{N-rGO}$ in sharp contrast to the paramagnetic behavior exhibited by the bare Ni_xP_y nanoclusters at low temperature. Thus, the N-rGO matrix supported Ni_xP_y manifests both electrocatalytic proficiency and magnetic ordering with potential application in the future green energy as well as in data storage technologies.

Graphic abstract

Keywords N-rGO supported Ni_xP_y · Electrocatalytic HER · Magnetic property

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1 Introduction

Present world witnessed a towering demand for clean energy techniques due to the constantly shrinking fossil fuel sources and ecological hazards caused by their burning [1–4]. Hydrogen has the potential to serve as an efficient agent for clean energy sources due to its super high calorific value [5]. Electrochemical reduction of water is considered as a simple as well as an effective method for hydrogen evolution reaction (HER) [6–8]. But two half reactions of the water electrolysis demand a high overpotential of more than 1.8 V instead of theoretically calculated 1.23 V with expected reaction rates [3, 9]. This is why the need for developing efficient catalysts is of much importance. Though platinum has been used as the most efficient electrocatalyst, limited availability and high price lead to the search of cost effective and efficient series of electrocatalysts for HER [10, 11]. With the emergence of graphene 2D materials took the center stage as promising electrocatalyst [12–16] due to their unique electronic, physical and chemical properties [17]. Also the search for non-noble metal based and earth abundant low cost alternatives has led to the development of transition metal based 2D materials like chalcogenides [18–20], carbides [21, 22], hydroxides [23, 24] and phosphides [25–30] as promising agents for electrochemical water splitting. Among them, Co and Ni based phosphides emerged as excellent electrocatalysts due to their high catalytic activity and stability in the acid medium [31]. Also, the nitrogen doped rGO attachment help enhancing the HER performance of phosphide 2D structure [32]. Generally, nickel phosphide exists in variety of phases Ni_3P , Ni_2P , Ni_5P_2 , Ni_{12}P_5 and Ni_5P_4 . Studies also suggest that phase and morphology play a crucial role in electrocatalytic HER activity [10]. There are several studies dealing with the HER performance of nickel phosphide [33–36], but studies are rare where mixed phase nickel phosphide has been employed to achieve both the goal of an efficient electrocatalyst as well as a promising magnetic storage device. Also the limited availability of the literatures studying the magnetic behaviour of nickel phosphides, having multiple phases, makes it difficult to come to a specific conclusion regarding the effect of various nickel phosphide phases on its magnetic nature. The study on how the formation of composites of nickel phosphide with other layered materials changes its magnetic property is still not reported in a comprehensive way according to the best of our knowledge. Pan et al reported ferromagnetic behaviour of Ni_2P NP at 5 K with saturation magnetization 0.065 emu/g and HER activity with Tafel slope 83.3 mV dec⁻¹ [6]. Reduced graphene oxide is a

well-established matrix element and also gathered attention for magnetic study by doping nitrogen via facile route of ammonia treatment during reduction process [37].

In the present work mixed phase nickel phosphide with metal rich Ni_2P and Ni_5P_4 phases has been synthesized successfully by anchoring it on the nitrogen doped reduced graphene oxide. Mixed phase nickel phosphide Ni_xP_y has been synthesized through a two-step hydrothermal and solid phase reaction in a facile and cost effective manner. The easy to execute synthesis route has given it the edge over chemical vapour deposition [38] and microwave synthesis [39] of TMD phosphides. The temperature control and carefully chosen Ni:P ratio were aimed at delivering a well-defined mixed phase nickel phosphide nanostructure. Graphene Oxide has been reduced and attached with as prepared Ni_xP_y through hydrothermal route in ammonia atmosphere in order to dope nitrogen. The structural, chemical and morphological analysis of the Ni_xP_y and its composite with nitrogen doped graphene oxide (N-rGO) has been systematically carried out. The hydrogen evolution reaction activity of the samples has been tested and the enhancement of the reaction rate has been observed in $\text{Ni}_x\text{P}_y/\text{N-rGO}$ in comparison with Ni_xP_y with satisfactory stability. Magnetization also witnessed a notable enhancement in the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite and exhibited ferromagnetic behaviour at 5 K while the bare Ni_xP_y exhibited super paramagnetic $M-H$ behaviour at that temperature. The enhancement in both HER activity and magnetic property can be attributed to the well attachment of N-rGO with Ni_xP_y where the former played the role on evolving specific dominant crystalline planes of Ni_2P and Ni_5P_4 out of several lattice planes present in the Ni_xP_y . Also, the presence of the metal rich phases like Ni_2P and Ni_5P_4 in Ni_xP_y has contributed beneficially in producing high magnetic moment and ferromagnetic behaviour at low temperature in $\text{Ni}_x\text{P}_y/\text{N-rGO}$.

2 Experimental section

2.1 Synthesis of $\text{Ni}_x\text{P}_y/\text{N-rGO}$

2.1.1 Synthesis of Ni_xP_y

All the chemicals were purchased from Sigma Aldrich and used as received. Ni_xP_y was synthesized by a facile hydrothermal technique followed by solid state reaction. First NiCl_2 and NaOH were taken in 1:2 molar ratio in order to prepare $\text{Ni}(\text{OH})_2$. The metal precursor and the NaOH were dissolved in DI water separately. Both solution were put on a magnetic stirrer and after 30 min the NaOH solution was added dropwise in the NiCl_2 solution

under stirring condition. The mixed solution was allowed to stir for another 10 min and then the entire solution was transferred to a stainless steel autoclave and kept at 150 °C for 18 h. Then the autoclave was cooled down to room temperature and the colloid solution was centrifuged and washed several times. The washed solution was dried at 60 °C overnight and the green colour as prepared $\text{Ni}(\text{OH})_2$ powder was obtained.

In the next step, Ni_xP_y was prepared by mixing $\text{Ni}(\text{OH})_2$ and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in a molar ratio of 1:5. The mixing was done through proper grinding and the ground powder was kept in a porcelain crucible and it was put in a tube furnace and kept at 330 °C for 2 h under a constant flow of nitrogen gas. Then the mixed powder was allowed to cool naturally, and the appeared sponge like porous structure was crushed to get a fine powder. The obtained powder was centrifuged and washed several times to remove unreacted salts. Then the powder was dried at 50 °C to obtain the as prepared Ni_xP_y .

2.1.2 Synthesis of $\text{Ni}_x\text{P}_y/\text{N-rGO}$

Again, 300 mg of as prepared Ni_xP_y and 10 mg of Graphene Oxide (GO) prepared through modified Hummers method [40] were separately taken in DI water solutions. The later was sonicated for 2 h and added dropwise to the metal hydroxide solution under the stirring condition and 10 ml ammoniacal water was also added during this process to achieve nitrogen doping. The entire solution was allowed to stir for 15 min. Then the whole solution was transferred to a stainless steel autoclave and kept at 200 °C for 24 h. The autoclave was further allowed to cool at room temperature, and the solution was centrifuged and washed several times. The washed solution was kept in normal room temperature to dry and the as prepared $\text{Ni}_x\text{P}_y/\text{N-rGO}$ was collected in black powder form. The same process was followed except the adding of Ni_xP_y to prepare nitrogen doped rGO (N-rGO). The whole process of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ synthesis is schematically depicted in Scheme 1.

2.2 Characterization

Rigaku Mini-Flex X-Ray diffractometer having Cu K α radiation ($k = 1.54178 \text{ \AA}$) source was used for the structural analysis of the samples. Raman spectroscopy was carried out in the Horiba T64000 with 514.5 nm laser source. Morphological analysis was done with the help of MERLIN (Carl Zeiss) Scanning Electron Microscopy and JEM 2100 Transmission Electron Microscope. ULVAC-PHI5000 Versa Probe II spectrometer equipped with Al K α radiation source of photon energy 1486.6 eV was employed for the XPS analysis.

Scheme 1 The synthesis steps for the final product of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ towards HER application

2.3 Magnetic measurement

DC magnetization measurements were performed using a Quantum Design SQUID magnetometer [magnetic property measurement system (MPMS) XL 7, Ever-cool model] in the temperature (T) range 5–300 K.

2.4 Electrochemical measurement

Epsilon (BASi) electrochemical work station was used to measure the electrochemical activity of the as prepared samples. Pt wire was used as a counter electrode, disc shape glassy carbon (GC) as the working electrode and Ag/AgCl saturated with KCl as the reference electrode. The working electrode surfaced was cleaned by ultrasonication in D.I water before the electrocatalyst loading. The electrocatalytic ink was prepared by dissolving 2 mg of the catalyst in a mixture of 130 μl water, 70 μl of isopropyl alcohol and 20 μl of 0.5% nafion. This solution was ultrasonicated for 30 min. The coating on the GCE was made by drop casting 10 μl of the as prepared ink with 1.34 mg/cm^2 sample loading. The linear sweep voltammetry was performed with 5 mV s^{-1} scan rate for HER measurements. The cyclic voltammetry sweeps were performed at different scan rates from 10 to 100 mV s^{-1} for the determination of the electrochemical active surface area (ECSA) with the help of electrochemical double layer capacitance (C_{dl}). Both the CV and LSV measurements were done in the acidic medium (0.5 M H_2SO_4 solution). The experimentally found overpotential was finally calibrated with the reversible hydrogen electrode (R.H.E). The electrochemical impedance spectroscopy was also performed in acidic medium (0.5 M H_2SO_4 solution) at an overpotential – 0.100 mV (RHE scale) from 0.1 Hz to 1 M Hz with Autolab.

3 Result and discussions

3.1 Structural, morphological and chemical analysis

The crystal structure and phases of as prepared N-rGO, Ni_xP_y along with $\text{Ni}_x\text{P}_y/\text{N-rGO}$ were shown in Fig. 1a. Figure 1a shows that Ni_xP_y consists of both hexagonal Ni_2P structure (PDF # 03-065-3544) and hexagonal Ni_5P_4 (PDF # 03-065-2075) structures [10]. The diffraction peaks at 44.6° , 47.3° and 54.3° are attributed to the (201), (210) and (300) crystal planes of Ni_2P [10]. Among them, (201) plane has been observed with notable increased intensity of diffraction peaks after attachment of nitrogen doped reduced graphene oxide (NrGO) with Ni_xP_y . The diffraction peaks at 28.7° , 30.4° , 31.5° , 34.7° , 36° , and 53° are attributed to (103), (200), (201), (202), (104) and (303) crystal planes of

Ni_5P_4 [10]. The diffraction peak of (303) plane has been observed in the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite with increased intensity. NrGO exhibits a broad diffraction peak of (002) plane between 20° and 30° due to the short range stacking in graphene sheets [41], a small diffraction peak can also be observed around 43° which represents the (100) plane. The faint appearance of the characteristic (002) diffraction peak in $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite suggests that well anchored Ni_xP_y hinders the restacking of rGO layers [42]. This corroborates that N-rGO has played a defining role in the emergence of two dominant crystal planes belonging to Ni_2P and Ni_5P_4 out of the various planes present in the Ni_xP_y . The slight shift of diffraction peaks of Ni_xP_y can be ascribed to the possible lattice stress produced due the attachment of N-rGO. The lower and higher angle shifts represent compressive and tensile stresses respectively. The Raman spectroscopy of as prepared rGO and $\text{Ni}_x\text{P}_y/\text{N-rGO}$ have also been carried out. In Fig. 1b, two intense peaks have been observed centered at around 1351.6 cm^{-1} and 1598.54 cm^{-1} in the rGO related to D band (due to the structural imperfection in A_{1g} mode) and G band (due to the first order scattering in E_{2g} mode) [32, 43]. No Raman peak related to Ni_xP_y is observed and this is expected from the earlier work [44]. D band to G band ratio increment to 1.011 in $\text{Ni}_x\text{P}_y/\text{N-rGO}$ from 0.995 in bare rGO suggests the formation of structural defects in N-rGO due to the successful nitrogen doping [43] which is also confirmed by the Raman spectroscopy of N-rGO (Fig. S1).

In addition, the slight red shift observed in the G band from 1598.54 cm^{-1} in rGO to 1585.54 cm^{-1} in $\text{Ni}_x\text{P}_y/\text{N-rGO}$ also serves as evidence of nitrogen doping in the carbon honeycomb structure in the hydrothermal process [45, 46]. Figure 2 shows the typical elemental mapping of the $\text{Ni}_x\text{P}_y/\text{N-rGO}$. The elemental mapping images in Fig. 2(a-f) confirm the uniform distribution of all the elements C, N, O, Ni and P over the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ nano composite structure.

Figure S2(a) represents the FESEM image of Ni_xP_y showing the small cluster type structures corroborated by the TEM image in Fig. S2(b). The elemental mappings of Ni and P in Fig. S2(c-d) also exhibit homogeneous distribution over as prepared structure. The selected area electron diffraction (SAED) image in Fig. S3 shows that the major diffraction rings of Ni_xP_y indicate the presence of both hexagonal Ni_2P with (111) and (211) crystal planes [10, 47] and hexagonal Ni_5P_4 with (110) crystal plane [48]. This suggests a formation of nickel rich mixed phase phosphide.

Also, the corresponding atomic structures and concerned crystal planes have been shown for both hexagonal Ni_2P (CIF # 1537576) and Ni_5P_4 (CIF # 2214342) in Fig. S3. Figure 3a shows the FESEM image of Ni_xP_y tinynanospheres anchored on the nitrogen doped rGO sheets. TEM image in Fig. 3b also supports the findings of the FESEM. Lattice fringe spacing, shown in Fig. 3c, d, of 0.187 nm and

Fig. 1 Characterization of samples: X-ray diffraction pattern of as prepared **a** Ni_xP_y , $\text{Ni}_x\text{P}_y/\text{N-rGO}$ and N-rGO and **b** Raman spectroscopy of rGO and $\text{Ni}_x\text{P}_y/\text{N-rGO}$

Fig. 2 Elemental mapping of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ nanocomposite: **a** showing the selected structure; **b** C, **c** N; **d** O; **e** Ni and **f** P

Fig. 3 Morphological analysis of $\text{Ni}_x\text{P}_y/\text{N-rGO}$: **a** FESEM of $\text{Ni}_x\text{P}_y/\text{N-rGO}$; **b** TEM of $\text{Ni}_x\text{P}_y/\text{N-rGO}$; **c** HRTEM of Ni_2P and **d** HRTEM of Ni_5P_4

0.309 nm are indexed to the (210) and (103) crystal surfaces corresponding to hexagonal Ni_2P and Ni_5P_4 [47, 48]. The SAED pattern in Fig. S4 of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ has shown the existence of the same crystal planes found from the d value calculation of the lattice planes. The related atomic structures, as well as the planes, have also been shown in the Fig. S4 using the CIF files mentioned earlier. This further corroborates the existence of the mixed phases

of nickel phosphide comprising of Ni_2P and Ni_5P_4 in the $\text{Ni}_x\text{P}_y/\text{N-rGO}$. The SEM image of sheet like N-rGO also proves the successful reduction of GO (Fig. S5).

3.2 XPS analysis

The chemical composition as well as chemical valence states of as synthesized Ni_xP_y and $\text{Ni}_x\text{P}_y/\text{N-rGO}$ have been

investigated with X-ray photoelectron spectroscopy (XPS). In Fig. 4a, the survey spectra confirm the presence of Ni, P, C, O and N in the $\text{Ni}_x\text{Py}/\text{N-rGO}$ composite. The high resolution binding energy spectra for Ni in Fig. 4b shows peaks at 853.7, 857.9, 872.1 and 880 eV are attributed to

$\text{Ni}2p_{3/2}$, the satellite peak of $\text{Ni}2p_{3/2}$, $\text{Ni}2p_{1/2}$ and satellite peak of $\text{Ni}2p_{1/2}$ states respectively [49]. The $\text{Ni}2p_{3/2}$ peak at 853.7 eV is very close to the binding energy peak of metallic Ni (852.6 eV) [47] suggesting a very small positive charge in Ni species of Ni_xPy which is the $\text{Ni}^{\delta+}$ state

Fig. 4 X-ray photoelectron spectroscopy analysis of $\text{Ni}_x\text{Py}/\text{N-rGO}$: **a** survey scan of $\text{Ni}_x\text{Py}/\text{N-rGO}$; high resolution scan of: **b** Ni; **c** P; **d** C; **e** N and **f** O

($0 < \delta < 2$). Further on careful analysis of the binding energy peaks of Ni in $\text{Ni}_x\text{P}_y/\text{N-rGO}$, a slight shift to the higher binding energy has been observed with respect to that of Ni in Ni_xP_y . This indicates an increase in the positive charge amount in Ni species after the formation of the composite [47]. Binding energy peak at 129.56 eV for the high resolution XPS spectra of P has been observed in Fig. 4c which corresponds to the P2p state, which is very close to the binding energy of elemental P (130.0 eV) [47]. This further suggests

The existence of a small negative charge in the P species of Ni_xP_y corresponds to P^{5-} state ($0 < \delta < 1$). The slight lower shift in the XPS peak of P in $\text{Ni}_x\text{P}_y/\text{N-rGO}$ in comparison with that of in Ni_xP_y indicates an increase in the negative charge of P in the Ni_xP_y after forming a composite with rGO. This leads to an efficient charge transfer mechanism from Ni to P [49]. High resolution XPS asymmetric spectrum of C for $\text{Ni}_x\text{P}_y/\text{N-rGO}$ in Fig. 4d with a well-known long tail towards higher binding energy side represents the sp^2 hybridized C=C bonding peak at 284.4 eV [50]. Additional binding energy peaks emerged due to the deconvolution appear at 287.8 and 285.8 eV correspond to the C=O [50] and C-N bonding [51]. The available π electrons due to the sp^2 hybridization elevate the donor density of rGO and also improve the plasmonic response. Due to the synergistic effect of these two factors, superior charge transfer takes place at the interface of electrode and electrolyte [52]. The strong peak intensity of the C=C bond exhibits a successful reduction of GO where as the C-N bonding is the evidence of efficient doping of nitrogen in the rGO of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite. Due to the very small amount of nitrogen doping, the high resolution XPS spectrum has a very low signal

to noise ratio. However the deconvolution of the spectrum of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ in Fig. 4e represents the binding energy spectra detected at 397.5, 398.9 and 400 eV. These peaks corresponding to pyridinic, pyrrolic and graphitic N species respectively further indicate the actual position of N in rGO [32]. The deconvoluted XPS spectra of O in Fig. 4f has been detected at 531.18 eV for both of the Ni_xP_y and $\text{Ni}_x\text{P}_y/\text{N-rGO}$, which is related to abundant surface hydroxyl (O-H) species [53]. The broad peak appeared at 532.8 eV presents C=O bond in $\text{Ni}_x\text{P}_y/\text{N-rGO}$ arising due to the presence of slightly unreduced GO and also the probable moisture adsorption under ambient condition [54].

3.3 Magnetic property study

The magnetic properties of the synthesized samples were characterized by temperature and field dependence of magnetization curves. Figure 5a–b shows that both the zero field cooled magnetization (M_{ZFC}) and field cooled magnetization (M_{FC}) curves at an applied field (H) of 100 Oe were measured in the heating cycle for Ni_xP_y , $\text{Ni}_x\text{P}_y/\text{N-rGO}$ and N-rGO (Fig. S5). Also, the field dependence of magnetization (M – H) has been studied at the temperatures 300 K and 5 K for Ni_xP_y , $\text{Ni}_x\text{P}_y/\text{N-rGO}$ and N-rGO and has been shown in the top insets of the Fig. 5a, b and Fig. (S6). The lower insets of the same Fig. 5a–b represent the magnetization (M – H) curves at low field region.

Figure 5a shows the M – T and M – H variations of as-prepared nano clustered structures of Ni_xP_y . Both the M_{ZFC} and M_{FC} curves are identical and no evidence of temperature dependent anomaly is found. Magnetic moments as evidenced from the M_{ZFC} and M_{FC} curves show a drastic

Fig. 5 Temperature (T) dependence of M_{ZFC} and M_{FC} curves: measured at $H=100$ Oe for **a** Ni_xP_y and **b** $\text{Ni}_x\text{P}_y/\text{N-rGO}$ respectively. The top insets show the field-dependent M – H curves at 300 and 5 K.

The bottom insets in **a** and **b** selectively reveal corresponding low field regions of the M – H curves measured at 300 and 5 K

increment with the gradual decrease of the temperature below 50 K. The observation indicates that the dominating paramagnetic component along with uncompensated surface spins contributed by both Ni_2P and Ni_5P_4 results a change in the magnetic order in Ni_xP_y . Bulk phases of metal rich nickel phosphides are known as Pauli paramagnets and exhibit a susceptibility that is independent of temperature [55], whereas crystalline nickel is strongly ferromagnetic [56]. The field dependence of M - H curves at 300 and 5 K are shown in the top inset of Fig. 5a. For both the temperatures, no magnetization saturation for Ni_xP_y was observed under an applied magnetic field up to 5 T. No hysteresis with nonlinear M - H behavior at 5 K suggests superparamagnetic ground state with progressive spin alignment along the external field. However, as shown in the bottom inset of Fig. 5a, a weak hysteresis loop of without saturation tendency is observed at 300 K exhibiting weak ferromagnetic behavior. The obtained coercivity (H_c) and remanence magnetization (M_R) are 108 Oe and 0.0028 emu/g, respectively.

Figure 5b displays the temperature variation of M_{ZFC} and M_{FC} of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite. A sharp increase in M_{FC} curve below 30 K has been observed with a further decrease of temperature down to 5 K, indicating a restoration of the ferromagnetic state from the paramagnetic state upon cooling. Moreover, M_{ZFC} curve behaves differently below 20 K as compare to M_{FC} . With the increase of temperature, M_{ZFC} first increases and reaches a maximum value at 15 K. Then it coincides with M_{FC} at 17 K, which is the blocking temperature (T_B) for this composite material. This behaviour of M - T predicts the large magnetic moment and also gathers support from the M - H curves shown in insets of Fig. 5b at 5 K. The existence of the strong hysteresis loop as shown in the bottom inset of Fig. 5b with coercivity $H_c = 1030$ Oe, remanence magnetization $M_R = 6.4$ emu/g and saturation magnetization $M_s = 35.1$ emu/g indicate the strong ferromagnetic character at 5 K. Though, in the upper inset of Fig. 5b, no hysteresis behavior is observed and a linear dependence of M with H indicates paramagnetic character at 300 K. Fig. S6 shows the M - T and M - H variation of nitrogen doped rGO (N-rGO). A large field-cooled effect is observed, where M_{ZFC} value remained smaller than the M_{FC} throughout the measured temperature range from 300 to 5 K. Below 35 K, M_{ZFC} and M_{FC} sharply increase with the gradual decrease of temperature. The field dependence of M (H) curves at 300 and 5 K are shown in insets of Fig. S6. At 300 K, shown in the inset of Fig. S6, the M - H curve shows a paramagnetic (PM) behavior with M varying linearly with H . However, M shows nonlinear variation of H with no signature of hysteresis at 5 K indicating predominant AFM ground state of the sample. The magnetic ordering of bare N-doped rGO can safely be discarded from the M - H and M - T results shown

in Fig S6. Here the attachment of the nitrogen doped rGO with Ni_xP_y plays a crucial role to enhance the magnetic moment contributed by Ni_2P and Ni_5P_4 phases, present in Ni_xP_y , by well orienting their unpaired spins at low temperature. This results the transition from paramagnetic behaviour of the Ni_xP_y to strong ferromagnetic nature of the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ at 5 K.

3.4 Hydrogen evolution reaction study

The hydrogen evolution reaction activity of the as synthesized N-rGO, Ni_xP_y and $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite have been investigated with a three electrode standard set up in 0.5 M H_2SO_4 electrolyte. The linear sweep voltammetry (LSV) curves of N-rGO, Ni_xP_y and $\text{Ni}_x\text{P}_y/\text{N-rGO}$ with the catalyst loading of 1.34 mg cm^{-2} on GCE have been shown in Fig. 6a without iR compensation. For comparison, LSV data of 20% Pt/C has been taken as a Ref. [57]. The overpotentials for reaching the 10 mA cm^{-2} current density were recorded as 248 and 265 mV for $\text{Ni}_x\text{P}_y/\text{N-rGO}$ and Ni_xP_y respectively.

This shows a satisfactory HER performance of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ at relatively low sample loading compared to MoS_2 [58], FePNPs@NPC [59], Ni_{12}P_5 hollow NPs, Ni_2P hollow NPs and Ni_5P_4 solid NPs [10] with respective sample loading of 5 mg cm^{-2} for the first two referred work and 1.99 mg cm^{-2} for the last referred work on the multiple nickel phosphide phases. Table S1 shows the satisfactory performance of the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ composite with a relatively low amount of sample loading in comparison with some other previously reported electrocatalysts for HER. This also implies the benefit of attaching N doped rGO with Ni_xP_y consisting of Ni_2P and Ni_5P_4 phases for improved electrochemical performance. It is noteworthy that just the physical mixing of Ni_xP_y and N-rGO, shown in Fig S12, is far behind the composite materials so far the electrocatalytic hydrogen evolution is concerned and it definitely establishes the synergistic benefit of the composite materials. For a detailed look at the mechanism of HER, Tafel plots have been derived from the LSV curves of Ni_xP_y and $\text{Ni}_x\text{P}_y/\text{N-rGO}$ by using Tafel equation

$$\eta = a + b \log j \quad (1)$$

where η is the overpotential, a is the intercept at overpotential axis, j is the cathodic current density and b is the Tafel slope. The Tafel slopes, shown in Fig. 6b, are determined as 83 and 156 dec^{-1} for $\text{Ni}_x\text{P}_y/\text{N-rGO}$ and Ni_xP_y indicates a faster HER rate for $\text{Ni}_x\text{P}_y/\text{N-rGO}$. For the purpose of comparison, the Tafel slope of 20% Pt has been showed [57]. The exchange current density at η_0 for the Ni_xP_y and $\text{Ni}_x\text{P}_y/\text{N-rGO}$ is calculated by extrapolating Tafel plot (Fig. 6b) and found to be increased from 209 to 282

Fig. 6 Electrochemical measurements: **a** LSV curves (without iR compensation) of the samples; **b** Tafel slopes; **c** chronoamperometry of the $\text{Ni}_x\text{P}_y/\text{N-rGO}$ for 1200 min and inset indicates durability test; **d** CV sweeps at different scan rates: for Ni_xP_y ; **e** $\text{Ni}_x\text{P}_y/\text{N-rGO}$ and **f** electrochemical double layer capacitance

$\mu\text{A cm}^{-2}$. The calculated exchange current density of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ is found to be superior to some previously reported noble metal free electrocatalysts [1, 60, 61]. The Tafel slope of $\text{Ni}_x\text{P}_y/\text{N-rGO}$ can compete well with the reported Tafel slopes of Ni_{12}P_5 , Ni_2P and Ni_5P_4 [10] with less amount of catalyst loading. $\text{Ni}_x\text{P}_y/\text{N-rGO}$ also shows a

faster HER activity than CoP [62] and Ni_2P [63]. Generally, in acidic media, there are three possible steps for the HER activity, the Volmer reaction

The Heyrovsky reaction,

and the Tafel reaction,

When Volmer reaction is fast and Heyrovsky and Tafel reactions are rate determining step, the Tafel slope is 30 or 40 mV dec⁻¹ [64]. When Volmer reaction plays the role of rate determining step, Tafel slope is about 120 mV dec⁻¹. In our study, the observed Tafel slope for Ni_xP_y/N-rGO indicates a fast Volmer step followed by the rate determining Heyrovsky step. Apart from catalytic activity, the stability of the catalyst in the acidic medium is another important factor. Here, the inset of Fig. 6c demonstrates the polarizing curve of Ni_xP_y/N-rGO after 2000 cycles run between -0.6 to 0.2 V with 100 mV s⁻¹ scan rate. It exhibits slight current density loss after 2000 cycles, which itself proves the excellent cycle life of Ni_xP_y/N-rGO in the acidic medium. Figure 6c shows the time dependent current density curve taken at the static overpotential 248 mV demonstrating that the catalyst retained its activity even after 1200 min. For gaining more insights on the electrocatalytic performance, electrochemical active surface area (ECSA), shown in Fig. 6d, e, f, has been calculated for Ni_xP_y and Ni_xP_y/N-rGO. The ECSA for the as prepared samples were determined by electrochemical double layer capacitance (*C_{dl}*). *C_{dl}* is believed to be positively proportional with ECSA [64]. *C_{dl}* is measured from the cyclic voltammetry curves, shown in Fig. 6d, e, in the non-faradic region (0 to 0.8 mV) since this region is considered for double layer capacitive behaviour. The difference of the current density of the CV sweeps at the midway overpotential taken at various scan rates (10 to 100 mV s⁻¹) were plotted and displayed in Fig. 6f. According to Fig. 6f, attachment of N-rGO with Ni_xP_y was clearly evident from the calculated *C_{dl}* value of 28.5 mF cm⁻² compared to 13 mF cm⁻² of Ni_xP_y. The corresponding ECSA calculation revealed an area of 65 cm² for Ni_xP_y and 142.5 cm² for Ni_xP_y/N-rGO (Method provided in Supplementary Information 1.1). The higher values of *C_{dl}*, as well as ECSA, indicate large surface area available to Ni_xP_y/N-rGO than Ni_xP_y helped the former to contribute with enhanced electrocatalytic activity. To gain further knowledge on the charge transfer mechanism, electrochemical impedance spectroscopy (EIS) has been done at -0.100 mV (RHE scale) overpotential with the frequency range from 1 MHz to 0.1 Hz. It is clearly visible from Nyquist plot in Fig. S7 that the Ni_xP_y/N-rGO has the smallest semi circle indicating a faster charge transfer mechanism. We propose a model equivalent circuit where the Ohmic resistance *R_s* is connected in series with a module comprising of a charge transfer resistance *R_{ct}*

and a constant phase element connected in parallel (Fig. S8). The *R_{ct}* values of Ni_xP_y/N-rGO, Ni_xP_y and N-rGO are 7.4, 8.2 and 9 Ω respectively which match well with the HER performance of the respective samples. The higher electrocatalytic surface area of the composite materials may be attributed to the synergistic effect of Ni₂P and Ni₅P₄ phases well anchored within N-rGO matrix. The HER activity was further analysed by calculating turnover frequency (TOF) which signifies the number of moles of water converted into H₂ by the no. of moles of active sites of the electrocatalyst with the assumption that each site took part in the reaction equally. The TOF values for Ni_xP_y and Ni_xP_y/N-rGO were calculated at 300 mV overpotential and found to be 0.011 s⁻¹ and 0.022 s⁻¹ (Method provided in Supplementary information 1.2). This also indicates the higher electrocatalytic activity of Ni_xP_y/N-rGO than Ni_xP_y. Also, according to some recent works, the higher catalytic performance of Ni_xP_y/N-rGO can be attributed to the presence of a metal center (δ⁺) and a pendant base P (δ⁻) situated close to it [10]. Our XPS study supports the presence of the metal center and pendant base which act as a hydride and proton acceptor respectively and in turn facilitate HER. Moreover, our XPS study also revealed that the formation of a composite of nitrogen doped rGO and mixed phase (both Ni₂P and Ni₅P₄) Ni_xP_y resulted in an increase of positive charge δ⁺ of the metal center as well as the negative charge δ⁻ of the pendant base. This, in turn, makes more availability of hydride acceptor and proton acceptor centers in Ni_xP_y/N-rGO, which initiate faster HER activity and large electrochemical active area for the composite. The SEM image (Fig. S9) of the Ni_xP_y/N-rGO collected from the electrode after the reaction showed no apparent morphological change and proved the robustness of the sample. The XRD analysis of the samples collected after durability test registered no apparent change in the crystal phases of the samples (Fig. S10). The similarity in signature peaks of Raman spectroscopy (Fig. S11) taken from the sample before and after durability test also proves the structural stability of the materials. The details analysis in Fig. S11 showed a small increase in D/G band ratio of the N-rGO in Ni_xP_y/N-rGO with the value 1.05 from 1.011. This can be ascribed to the fact that a slight reduction of N-rGO is likely to occur due to the exposure in the acidic electrolyte medium [65]. Both the XRD and Raman characterization of the as collected samples from electrode suggests the robustness of the Ni_xP_y/N-rGO electrocatalyst.

4 Conclusion

In this work, mixed phase nickel phosphide (Ni_xP_y) has been synthesized by two step hydrothermal synthesis followed by the solid state reaction under an inert

atmosphere. The as prepared sample was attached with in situ nitrogen doped reduced graphene oxide (rGO) through wet chemical route. The structural, chemical and morphological investigations were carried out with XRD, EDAX, XPS, Raman Spectroscopy, Elemental Mapping, FESEM and HRTEM. The Ni_xP_y supported by N-rGO matrix was proved to be beneficial for the performance of hydrogen evolution reaction in acid medium with appreciable durability. The magnetic transition from paramagnetic to ferromagnetic behaviour at low temperature was observed when Ni_xP_y was subjected to form composite with N-rGO. The well crystalline phases of Ni_xP_y and more available positive and negative charge centers to Ni and P after the formation of the composite were highly beneficial to establish Ni_xP_y /N-rGO as an efficient electrocatalyst as well as magnetic material with potential for application in both green energy generation and energy storage device.

5 Supporting information

Raman Spectroscopy of N-rGO; SEM, elemental mapping and TEM of Ni_xP_y ; Selected area electron diffraction of Ni_xP_y ; Selected area electron diffraction of Ni_xP_y /N-rGO; SEM of N-rGO; ECSA and TOF calculation method; Magnetic characteristic study of (M–T and M–H) N-rGO.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Li J, Li J, Zhou X, Xia Z, Gao W, Ma Y, Qu Y (2016) Highly efficient and robust nickel phosphides as bifunctional electrocatalysts for overall water-splitting. *ACS Appl Mater Interfaces* 8(17):10826–10834
- Chow J, Kopp RJ, Portney PR (2003) Energy resources and global development. *Science* 302(5650):1528–1531
- Qu Y, Duan X (2013) Progress, challenge and perspective of heterogeneous photocatalysts. *Chem Soc Rev* 42(7):2568–2580
- Desideri U, Yan J (2012) Clean energy technologies and systems for a sustainable world. *Appl Energy* 97:1–4
- Dresselhaus M, Thomas I (2001) Alternative energy technologies. *Nature* 414(6861):332
- Yan L, Jiang H, Xing Y, Wang Y, Liu D, Gu X, Dai P, Li L, Zhao X (2018) Nickel metal–organic framework implanted on graphene and incubated to be ultrasmall nickel phosphide nanocrystals acts as a highly efficient water splitting electrocatalyst. *J Mater Chem A* 6(4):1682–1691
- Jia Y, Zhang L, Gao G, Chen H, Wang B, Zhou J, Soo MT, Hong M, Yan X, Qian G (2017) A heterostructure coupling of exfoliated Ni–Fe hydroxide nanosheet and defective graphene as a bifunctional electrocatalyst for overall water splitting. *Adv Mater* 29(17):1700017
- Tang T, Jiang W-J, Niu S, Liu N, Luo H, Chen Y-Y, Jin S-F, Gao F, Wan L-J, Hu J-S (2017) Electronic and morphological dual modulation of cobalt carbonate hydroxides by Mn doping toward highly efficient and stable bifunctional electrocatalysts for overall water splitting. *J Am Chem Soc* 139(24):8320–8328
- Zeng K, Zhang D (2010) Recent progress in alkaline water electrolysis for hydrogen production and applications. *Prog Energy Combust Sci* 36(3):307–326
- Pan Y, Liu Y, Zhao J, Yang K, Liang J, Liu D, Hu W, Liu D, Liu Y, Liu C (2015) Monodispersed nickel phosphide nanocrystals with different phases: synthesis, characterization and electrocatalytic properties for hydrogen evolution. *J Mater Chem A* 3(4):1656–1665
- Arenz M, Stamenkovic V, Schmidt T, Wandelt K, Ross P, Markovic N (2002) CO adsorption and kinetics on well-characterized Pd films on Pt (111) in alkaline solutions. *Surf Sci* 506(3):287–296
- Askari MB, Salarizadeh P, Rozati SM, Seifi M (2019) Two-dimensional transition metal chalcogenide composite/reduced graphene oxide hybrid materials for hydrogen evolution application. *Polyhedron* 162:201–206
- Askari MB, Salarizadeh P (2019) Superior catalytic performance of NiCo_2O_4 nanorods loaded rGO towards methanol electro-oxidation and hydrogen evolution reaction. *J Mol Liq* 291:111306
- Salarizadeh P, Askari MB, Seifi M, Rozati SM (2019) MoS_2 coating on different carbonaceous materials: comparison of electrochemical properties and hydrogen evolution reaction performance. *J Electroanal Chem* 847:113198
- Askari MB, Salarizadeh P, Seifi M, Rozati SM (2019) Electrocatalytic properties of CoS_2 / MoS_2 /rGO as a non-noble dual metal electrocatalyst: the investigation of hydrogen evolution and methanol oxidation. *J Phys Chem Solids* 135:109103
- Askari MB, Salarizadeh P (2019) Ultra-small ReS_2 nanoparticles hybridized with rGO as cathode and anode catalysts towards hydrogen evolution reaction and methanol electro-oxidation for DMFC in acidic and alkaline media. *Synth Met* 256:116131
- Jin H, Guo C, Liu X, Liu J, Vasileff A, Jiao Y, Zheng Y, Qiao S-Z (2018) Emerging two-dimensional nanomaterials for electrocatalysis. *Chem Rev* 118(13):6337–6408
- Zhang X, Wu Y, Sun Y, Ding P, Liu Q, Tang L, Guo J (2018) Hybrid of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ nanocubes and MoS_2 nanosheets on nitrogen-doped graphene realizing improved electrochemical hydrogen production. *Electrochim Acta* 263:140–146
- Swesi AT, Masud J, Nath M (2016) Nickel selenide as a high-efficiency catalyst for oxygen evolution reaction. *Energy Environ Sci* 9(5):1771–1782
- Zhang X, Zhang Q, Sun Y, Zhang P, Gao X, Zhang W, Guo J (2016) MoS_2 -graphene hybrid nanosheets constructed 3D architectures with improved electrochemical performance for lithium-ion batteries and hydrogen evolution. *Electrochim Acta* 189:224–230
- Gao W, Shi Y, Zhang Y, Zuo L, Lu H, Huang Y, Fan W, Liu T (2016) Molybdenum carbide anchored on graphene nanoribbons as highly efficient all-pH hydrogen evolution reaction electrocatalyst. *ACS Sustain Chem Eng* 4(12):6313–6321
- Seh ZW, Fredrickson KD, Anasori B, Kibsgaard J, Strickler AL, Lukatskaya MR, Gogotsi Y, Jaramillo TF, Vojvodic A (2016)

- Two-dimensional molybdenum carbide (MXene) as an efficient electrocatalyst for hydrogen evolution. *ACS Energy Lett* 1(3):589–594
23. Liu X, Wang X, Yuan X, Dong W, Huang F (2016) Rational composition and structural design of in situ grown nickel-based electrocatalysts for efficient water electrolysis. *J Mater Chem A* 4(1):167–172
 24. Song F, Schenk K, Hu X (2016) A nanoporous oxygen evolution catalyst synthesized by selective electrochemical etching of perovskite hydroxide $\text{CoSn}(\text{OH})_6$ nanocubes. *Energy Environ Sci* 9(2):473–477
 25. Feng L, Xue H (2017) Advances in transition-metal phosphide applications in electrochemical energy storage and catalysis. *ChemElectroChem* 4(1):20–34
 26. Popczun EJ, McKone JR, Read CG, Biacchi AJ, Wiltout AM, Lewis NS, Schaak RE (2013) Nanostructured nickel phosphide as an electrocatalyst for the hydrogen evolution reaction. *J Am Chem Soc* 135(25):9267–9270
 27. Li G, Wang J, Yu J, Liu H, Cao Q, Du J, Zhao L, Jia J, Liu H, Zhou W (2020) Ni-Ni₃P nanoparticles embedded into N, P-doped carbon on 3D graphene frameworks via in situ phosphatization of saccharomycetes with multifunctional electrodes for electrocatalytic hydrogen production and anodic degradation. *Appl Catal B* 261:118147
 28. Song P, Wang H (2019) High-performance polymeric materials through hydrogen-bond cross-linking. *Adv Mater*. <https://doi.org/10.1002/adma.201901244>
 29. Yu J, Li G, Liu H, Zhao L, Wang A, Liu Z, Li H, Liu H, Hu Y, Zhou W (2019) Ru–Ru₂P/NPC and NPC@ RuO₂ synthesized via environment-friendly and solid-phase phosphating process by saccharomycetes as N/P sources and carbon template for overall water splitting in acid electrolyte. *Adv Funct Mater* 29(22):1901154
 30. Li G, Yu J, Jia J, Yang L, Zhao L, Zhou W, Liu H (2018) Cobalt-cobalt phosphide nanoparticles@ nitrogen-phosphorus doped carbon/graphene derived from cobalt ions adsorbed saccharomycete yeasts as an efficient, stable, and large-current-density electrode for hydrogen evolution reactions. *Adv Funct Mater* 28(40):1801332
 31. Wang H, Xie Y, Cao H, Li Y, Li L, Xu Z, Wang X, Xiong N, Pan K (2017) Flower-like nickel phosphide microballs assembled by nanoplates with exposed high-energy (0 0 1) facets: efficient electrocatalyst for the hydrogen evolution reaction. *Chemsuschem* 10(24):4899–4908
 32. Zhang X, Li J, Sun Y, Li Z, Liu P, Liu Q, Tang L, Guo J (2018) N-doped reduced graphene oxide supported mixed Ni₂PCoP realize efficient overall water electrolysis. *Electrochim Acta* 282:626–633
 33. Liu C, Gong T, Zhang J, Zheng X, Mao J, Liu H, Li Y, Hao Q (2020) Engineering Ni₂P–NiSe₂ heterostructure interface for highly efficient alkaline hydrogen evolution. *Appl Catal B* 262:118245
 34. Veeramani V, Matsagar BM, Yamauchi Y, Badjah AY, Naushad M, Habila M, Wabaidur S, Allothman ZA, Wang Z-L, Wu KC-W (2019) Metal organic framework derived nickel phosphide/graphitic carbon hybrid for electrochemical hydrogen generation reaction. *J Taiwan Inst Chem Eng* 96:634–638
 35. Li J, Li S, Pu J, Zhong C, Zhou Q, Shen Z, Zhang H, Ma H (2020) Electronic modulation of nickel phosphide by iron doping and its assembly on a graphene framework for efficient electrocatalytic water oxidation. *J Alloys Compd* 824:153913
 36. Yu X, Yu Z-Y, Zhang X-L, Zheng Y-R, Duan Y, Gao Q, Wu R, Sun B, Gao M-R, Wang G (2019) “Superaerophobic” nickel phosphide nanoarray catalyst for efficient hydrogen evolution at ultrahigh current densities. *J Am Chem Soc* 141(18):7537–7543
 37. Liu Y, Feng Q, Tang N, Wan X, Liu F, Lv L, Du Y (2013) Increased magnetization of reduced graphene oxide by nitrogen-doping. *Carbon* 60:549–551
 38. Panneerselvam A, Malik MA, Afzaal M, O'Brien P, Helliwell M (2008) The chemical vapor deposition of nickel phosphide or selenide thin films from a single precursor. *J Am Chem Soc* 130(8):2420–2421
 39. Hu X, Yu JC (2008) High-yield synthesis of nickel and nickel phosphide nanowires via microwave-assisted processes. *Chem Mater* 20(21):6743–6749
 40. Chakraborty S, Mukherjee A, Basu S (2018) RGO–MoS₂ supported NiCo₂O₄ catalyst toward solar water splitting and dye degradation. *ACS Sustain Chem Eng* 6(4):5238–5247
 41. Si Y, Samulski ET (2008) Exfoliated graphene separated by platinum nanoparticles. *Chem Mater* 20(21):6792–6797
 42. Jiang X, Yang X, Zhu Y, Shen J, Fan K, Li C (2013) In situ assembly of graphene sheets-supported SnS₂ nanoplates into 3D macroporous aerogels for high-performance lithium ion batteries. *J Power Sources* 237:178–186
 43. Youn HC, Bak SM, Kim MS, Jaye C, Fischer DA, Lee CW, Yang XQ, Roh KC, Kim KB (2015) High-surface-area nitrogen-doped reduced graphene oxide for electric double-layer capacitors. *Chemsuschem* 8(11):1875–1884
 44. Ge X, Li Z, Yin L (2017) Metal-organic frameworks derived porous core/shellCoP@ C polyhedrons anchored on 3D reduced graphene oxide networks as anode for sodium-ion battery. *Nano Energy* 32:117–124
 45. McAllister MJ, Li J-L, Adamson DH, Schniepp HC, Abdala AA, Liu J, Herrera-Alonso M, Milius DL, Car R, Prud'homme RK (2007) Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem Mater* 19(18):4396–4404
 46. Jin Z, Yao J, Kittrell C, Tour JM (2011) Large-scale growth and characterizations of nitrogen-doped monolayer graphene sheets. *ACS Nano* 5(5):4112–4117
 47. Zhou R, Zhang J, Chen Z, Han X, Zhong C, Hu W, Deng Y (2017) Phase and composition controllable synthesis of nickel phosphide-based nanoparticles via a low-temperature process for efficient electrocatalytic hydrogen evolution. *Electrochim Acta* 258:866–875
 48. Laursen A, Patraju K, Whitaker M, Retuerto M, Sarkar T, Yao N, Ramanujachary K, Greenblatt M, Dismukes G (2015) Nanocrystalline Ni₃P₄: a hydrogen evolution electrocatalyst of exceptional efficiency in both alkaline and acidic media. *Energy Environ Sci* 8(3):1027–1034
 49. Pan Y, Hu W, Liu D, Liu Y, Liu C (2015) Carbon nanotubes decorated with nickel phosphide nanoparticles as efficient nano-hybrid electrocatalysts for the hydrogen evolution reaction. *J Mater Chem A* 3(24):13087–13094
 50. Hsu H-C, Shown I, Wei H-Y, Chang Y-C, Du H-Y, Lin Y-G, Tseng C-A, Wang C-H, Chen L-C, Lin Y-C (2013) Graphene oxide as a promising photocatalyst for CO₂ to methanol conversion. *Nanoscale* 5(1):262–268
 51. Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruoff RS (2007) Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 45(7):1558–1565
 52. Saha S, Samanta P, Murmu NC, Kuila T (2017) Investigation of the surface plasmon polariton and electrochemical properties of covalent and non-covalent functionalized reduced graphene oxide. *Phys Chem Chem Phys* 19(42):28588–28595
 53. Pu Z, Xue Y, Li W, Amiin IS, Mu S (2017) Efficient water splitting catalyzed by flexible NiP₂ nanosheet array electrodes under both neutral and alkaline solutions. *New J Chem* 41(5):2154–2159
 54. Lee DU, Kim BJ, Chen Z (2013) One-pot synthesis of a mesoporous NiCo₂O₄ nanoplatelet and graphene hybrid and its oxygen reduction and evolution activities as an efficient bi-functional electrocatalyst. *J Mater Chem A* 1(15):4754–4762

55. Brock SL, Senevirathne K (2008) Recent developments in synthetic approaches to transition metal phosphide nanoparticles for magnetic and catalytic applications. *J Solid State Chem* 181(7):1552–1559
56. Leslie-Pelecky DL, Rieke RD (1996) Magnetic properties of nanostructured materials. *Chem Mater* 8(8):1770–1783
57. Wang X, Li W, Xiong D, Petrovykh DY, Liu L (2016) Bifunctional nickel phosphide nanocatalysts supported on carbon fiber paper for highly efficient and stable overall water splitting. *Adv Funct Mater* 26(23):4067–4077
58. Li Y, Wang H, Xie L, Liang Y, Hong G, Dai H (2011) MoS₂ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. *J Am Chem Soc* 133(19):7296–7299
59. Wang T, Liu L, Zhu Z, Papakonstantinou P, Hu J, Liu H, Li M (2013) Enhanced electrocatalytic activity for hydrogen evolution reaction from self-assembled monodispersed molybdenum sulfide nanoparticles on an Au electrode. *Energy Environ Sci* 6(2):625–633
60. Mukherjee A, Chakrabarty S, Su W-N, Basu S (2018) Nanostructured nickel ferrite embedded in reduced graphene oxide for electrocatalytic hydrogen evolution reaction. *Mater Today Energy* 8:118–124
61. Wang X, Kolen'ko YV, Bao XQ, Kovnir K, Liu L (2015) One-step synthesis of self-supported nickel phosphide nanosheet array cathodes for efficient electrocatalytic hydrogen generation. *Angew Chem Int Ed* 54(28):8188–8192
62. Jiang P, Liu Q, Ge C, Cui W, Pu Z, Asiri AM, Sun X (2014) CoP nanostructures with different morphologies: synthesis, characterization and a study of their electrocatalytic performance toward the hydrogen evolution reaction. *J Mater Chem A* 2(35):14634–14640
63. Feng L, Vrabel H, Bensimon M, Hu X (2014) Easily-prepared dinickel phosphide (Ni₂P) nanoparticles as an efficient and robust electrocatalyst for hydrogen evolution. *Phys Chem Chem Phys* 16(13):5917–5921
64. Pan Y, Lin Y, Liu Y, Liu C (2016) Size-dependent magnetic and electrocatalytic properties of nickel phosphide nanoparticles. *Appl Surf Sci* 366:439–447
65. Hayes WJ, Joseph P, Mughal MZ, Papakonstantinou P (2015) Production of reduced graphene oxide via hydrothermal reduction in an aqueous sulphuric acid suspension and its electrochemical behaviour. *J Solid State Electrochem* 19(2):361–380

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