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## *In situ* growth of NiSe<sub>2</sub> nanoparticles on g-C<sub>3</sub>N<sub>4</sub> nanosheets for an efficient hydrogen evolution reaction†

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A safe, non-precious, and low-cost catalyst, having a high hydrogen evolution rate, is one of the key demands for a sustainable hydrogen economy. In this study, we used a low-cost hydrothermal technique to prepare a NiSe<sub>2</sub> nanoparticle-based catalyst. These particles were grown on 2D g-C<sub>3</sub>N<sub>4</sub> nanosheets to improve their physical and chemical properties. The synthesized NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite catalyst demonstrated a high HER performance when compared to bare NiSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. Specifically, the NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite demonstrated a lower Tafel slope of 64 mV dec<sup>-1</sup>, a stable HER up to 1000 min, and a low overpotential of 87 mV at a current density of 10 mA cm<sup>-2</sup>. The superior HER performance of the composite on 2D g-C<sub>3</sub>N<sub>4</sub> corresponds to high active sites, and the synergistic interfacial contact leads to enhanced conductivity for rapid charge transport and long chemical stability. Thus, our study offers a pathway for the synthesis and development of non-precious, non-toxic, and highly stable electrocatalysts to replace noble metal-based catalysts and reduce the production costs of H<sub>2</sub> gas.

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## 1. Introduction

The depletion of fossil fuels and accompanying environmental damage, requires a search for a new and unconventional energy source.<sup>1</sup> Hydrogen has emerged as an optimal solution for tackling the escalating energy and environmental challenges faced globally. The energy density of hydrogen is about 140 MJ kg<sup>-1</sup>, which is nearly three times that of gasoline (46.5 MJ kg<sup>-1</sup>).<sup>2</sup> Hydrogen is produced using different technologies such as photolysis, electrolysis, or thermolysis. Electrocatalytic water splitting, one of the major energy study fields, has been under intense development by researchers to produce a high yield of H<sub>2</sub> gas with an acceptable energy and cost consumption. Using suitable electrocatalysts, the water splitting leads to the hydrogen evolution reaction (HER). An ideal electrocatalyst should increase the

faradaic efficiency, speed up the reaction kinetics, reduce ohmic losses, and work in different pH conditions. Extensive research has revealed a wide range of electrocatalysts that catalyze these critical reactions. Currently, platinum (Pt) and Pt-based electrodes show a very high catalytic performance and stability for HER. However, their commercial application is constrained by their high price and limited availability. Overall, there is an urgent requirement to develop state-of-the-art, high-performance, non-precious metal-based electrocatalysts for electrocatalytic H<sub>2</sub> generation.<sup>3-7</sup>

Recently, earth-abundant<sup>8</sup> transition metal-based chalcogenides,<sup>9</sup> hydroxides, phosphides,<sup>10</sup> carbides, nitrides, metal-organic-frameworks (MOF),<sup>11</sup> are being investigated for their HER activities. The chalcogenides are anticipated to be more covalent, have smaller band gaps, and offer better band alignment with water redox levels than their counterparts, allowing for more effective charge transfer and improved catalytic efficiency. Among chalcogenides, nickel selenide (NiSe<sub>2</sub>) exhibits a relatively superior electrochemical catalytic activity, chemical stability, low toxicity, and bio-compatibility. However, particle agglomeration and low electrical conductivity lead to a low HER performance because of the sluggish charge kinetics, which need to be resolved.<sup>12,13</sup>

Several strategies have been utilized to improvise the electrochemical activity of NiSe<sub>2</sub>. Some examples include nano-structurization,<sup>14</sup> dual-anion doping,<sup>15</sup> doping,<sup>16</sup> interfacial

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engineering.<sup>16,17</sup> In particular, 2D-based layered materials offer greater potential for different electrochemical applications.<sup>18</sup> Graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) offers simple synthesis, excellent stability, a 2D layered structure, and a tunable molecular structure for heterogeneous electrocatalysts.<sup>19,20</sup> The  $\text{g-C}_3\text{N}_4$  enhances the interaction with materials by providing N sites, resulting in abundant active sites, optimized electronic states, and rapid mass/charge transfer.<sup>21,22</sup>

Different research groups have utilized  $\text{g-C}_3\text{N}_4$  to design heterostructures for enhancing the electrocatalytic HER activity. Guan *et al.* synthesized a  $\text{MoS}_2/\text{g-CN}$  heterostructure that demonstrated an overpotential of 141 mV at 10 mA cm<sup>-2</sup> and a Tafel slope of 57 mV dec<sup>-1</sup>.<sup>23</sup> In another report, Zulqarnain *et al.*  $\text{FeCoSe}_2/\text{g-C}_3\text{N}_4$  was found to show an HER at an overpotential of 83 mV at 20 mA cm<sup>-2</sup> and a current density of 14.80 mA cm<sup>-2</sup> at 0 V (vs. RHE),<sup>24</sup> which was considerably greater when compared to bare  $\text{FeCoSe}_2$ . Other researchers studied  $\text{g-C}_3\text{N}_4/\text{MoS}_2$ ,<sup>25</sup> holey  $\text{g-C}_3\text{N}_4$  supported single-atom catalysts (SACs),<sup>26</sup>  $\text{FeSe}_2/\text{g-C}_3\text{N}_4$ ,<sup>27</sup>  $\text{MoB}/\text{g-C}_3\text{N}_4$ ,<sup>28</sup>  $\text{C}_3\text{N}_4@\text{MoN}$ ,<sup>29</sup>  $\text{g-C}_3\text{N}_4/\text{C}$ ,<sup>30</sup>  $\text{FeSe}_2/\text{g-C}_3\text{N}_4$ <sup>31</sup> and demonstrated the role of  $\text{g-C}_3\text{N}_4$  in improving the HER properties of compounds. Thus, it is expected that hetero-structuring of  $\text{g-C}_3\text{N}_4$  with  $\text{NiSe}_2$  can effectively improve the electrochemical properties of  $\text{NiSe}_2$  to give a high-performance HER.

Herein, we have grown  $\text{NiSe}_2$  on  $\text{g-C}_3\text{N}_4$  nanosheets to form a  $\text{NiSe}_2/\text{g-C}_3\text{N}_4$  nanocomposite using a hydrothermal method. The N-sites of  $\text{g-C}_3\text{N}_4$  during the hydrothermal process interacted synergistically with  $\text{NiSe}_2$  to improve the electrical conductivity, active surface area, and charge kinetics. The prepared electrocatalyst exhibited excellent HER activity with a smaller overpotential of 87 mV to give a current density of 10 mA cm<sup>-2</sup>, a reduced Tafel slope of 64 mV dec<sup>-1</sup>, and a long-time stable HER activity up to 1000 min.

## 2. Experimental details

### 2.1. Materials

The high purity chemicals were utilized without further purification. Melamine, hydrazine hydrate, nickel(II) acetate tetrahydrate, and *N*-methyl-2-pyrrolidinone (NMP), selenium powder (Se), acetylene black and polyvinylidene fluoride (PVDF) were purchased from Sigma-Aldrich Chemical Reagent Co. Ltd.

### 2.2. Preparation of $\text{g-C}_3\text{N}_4$

Using a previously reported method,<sup>32</sup> bulk  $\text{g-C}_3\text{N}_4$  was synthesized using the thermal polycondensation of melamine.<sup>33,34</sup> To achieve this, 5 g of melamine was heated in an alumina crucible under an air environment, until it gradually reached 550 °C (5 °C min<sup>-1</sup>). After a 4 h heating period, the mixture was cooled naturally to room temperature and ground in a mortar, to form a yellow bulk  $\text{g-C}_3\text{N}_4$  powder. It was then transferred to an alumina crucible and subjected to a heating process in a nitrogen environment. The temperature was raised to 500 °C (5 °C min<sup>-1</sup>)/2 h. Finally, the obtained mixture was cooled

naturally to ambient temperature, resulting in the formation of light yellow layered  $\text{g-C}_3\text{N}_4$  nanosheet powder.

### 2.3. Preparation of $\text{NiSe}_2/\text{g-C}_3\text{N}_4$

In a typical synthesis, an equal volume ratio of  $\text{g-C}_3\text{N}_4$  nanosheets and deionized (DI) water was subjected to ultrasonication at room temperature for 1 h. The resulting solution was centrifuged at 2500 rpm/5 min, and the supernatant collected was a  $\text{g-C}_3\text{N}_4$  nanosheet suspension. Next, a mixture was prepared by combining 2 mmol of nickel acetate, 2 mmol of selenium powder, and 20 mL of  $\text{g-C}_3\text{N}_4$  nanosheet suspension (1 mg mL<sup>-1</sup>) in 50 mL of DI water. The mixture was stirred (800 rpm) for 20 min followed by dropwise addition of 20 mL of hydrazine. The solution was introduced into a hydrothermal reactor with a volume of 100 mL and held at a temperature of 180 °C for 12 h. To eliminate containments, the resulting precipitate underwent multiple washings using DI water and ethanol. The deep-gray precipitate was collected and dried overnight in vacuum oven at 80 °C to produce the  $\text{NiSe}_2/\text{g-C}_3\text{N}_4$  nanocomposite.<sup>5</sup>

### 2.4. Measurement of the catalytic activity towards the HER

The electrocatalytic properties of prepared materials were measured using a PGSTAT302N electrochemical workstation (Metrohm Autolab), in a three-electrode configuration at room temperature. The setup consists of Hg/HgO (reference), graphite rod (counter) and synthesized material (working) electrodes in an aqueous 1 M KOH electrolyte. The active electrode was prepared by drop-casting the active catalyst (2 mg) in 5 wt% Nafion (15 µL) and isopropanol (2 mL) onto the 1 × 1 cm<sup>2</sup> nickel foam (NF). Prior to the electrochemical analysis, cyclic voltammetry (CV) was carried out for 50 cycles in the potential window of 1 V to 1.6 V vs. RHE. The linear sweep voltammetry (LSV) curves acquired were adjusted using the iR compensation at a scan rate of 10 mV s<sup>-1</sup>. Electrical impedance spectroscopy (EIS) was carried out in the frequency range of 1 MHz to 100 mHz, and chronoamperometry was carried out to measure the stability. The reversible hydrogen electrode (RHE) scale was utilized for standardizing LSV potential values using, *E* vs. RHE = *E* vs. Hg/HgO + 0.950 V. To compute the electrical double layer capacitance (*C*<sub>dl</sub>), in the potential range of 0 to 0.2 V vs. RHE, the scan speeds in CV curves were varied from 5 to 50 mV s<sup>-1</sup>.

### 2.5. Material characterization

The physicochemical characteristics of the synthesized materials were investigated using different characterization techniques. X-ray diffraction (XRD, Rigaku Ultima IV) using CuK $\alpha$  radiation ( $\lambda = 0.15406$  nm) was used for the phase configuration and structural details. The field emission scanning electron microscopy (FE-SEM, Jeol JSM-7900F, Japan), was utilized for understanding surface morphological characteristics. A spectrophotometer (Bruker, USA) was used to perform Fourier transform infrared (FTIR) spectroscopy. Selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HR-TEM) were performed using a Jeol JEM-2200FS. A K-alpha X-ray spectrometer was used for the X-ray



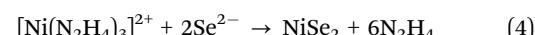
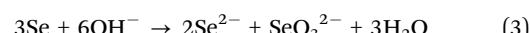
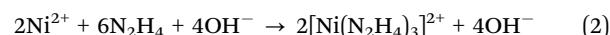
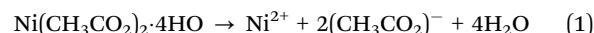
photoelectron spectroscopy (XPS) investigation. The contact angles were measured with respect to standard liquids with a Rame-Hart goniometer.

### 3. Results and discussion

#### 3.1. Reaction and growth mechanism

The possible reaction mechanism for the formation of  $\text{NiSe}_2$  and  $\text{NiSe}_2/\text{g-C}_3\text{N}_4$  was explained by chemical reactions. First, the ionic dissociation of nickel acetate in the reactant solution takes place (see eqn (1)). In the presence of the strong reducing agent, hydrazine hydrate,  $\text{Ni}^{2+}$  is reduced forming an intermediate complex (see eqn (2)). Moreover, the highly basic hydrazine hydrate and the temperature inside hydrothermal treatment promote the dissolution of the Se powder in DI water to form  $\text{Se}^{2-}$  and  $\text{SeO}_3^{2-}$  ions (eqn (3)). The used hydrazine

hydrate controls the pH and release of the  $\text{Se}^{2-}$  ions. The used  $\text{Ni}:\text{Se}$  precursor ratio was 1:2, so the final product should be a diselenide. These  $\text{Se}^{2-}$  ions will react with the Ni complex to form  $\text{NiSe}_2$  (the desired product, see eqn (4)).



To form the composite, a similar procedure was used with addition of  $\text{g-C}_3\text{N}_4$  during the hydrothermal treatment. The  $\text{g-C}_3\text{N}_4$  nanosheets provide enormous active sites for  $\text{NiSe}_2$  nanoparticles to grow. To reduce the reaction energy, these particles tend to aggregate which leads to self-assembly and anisotropic

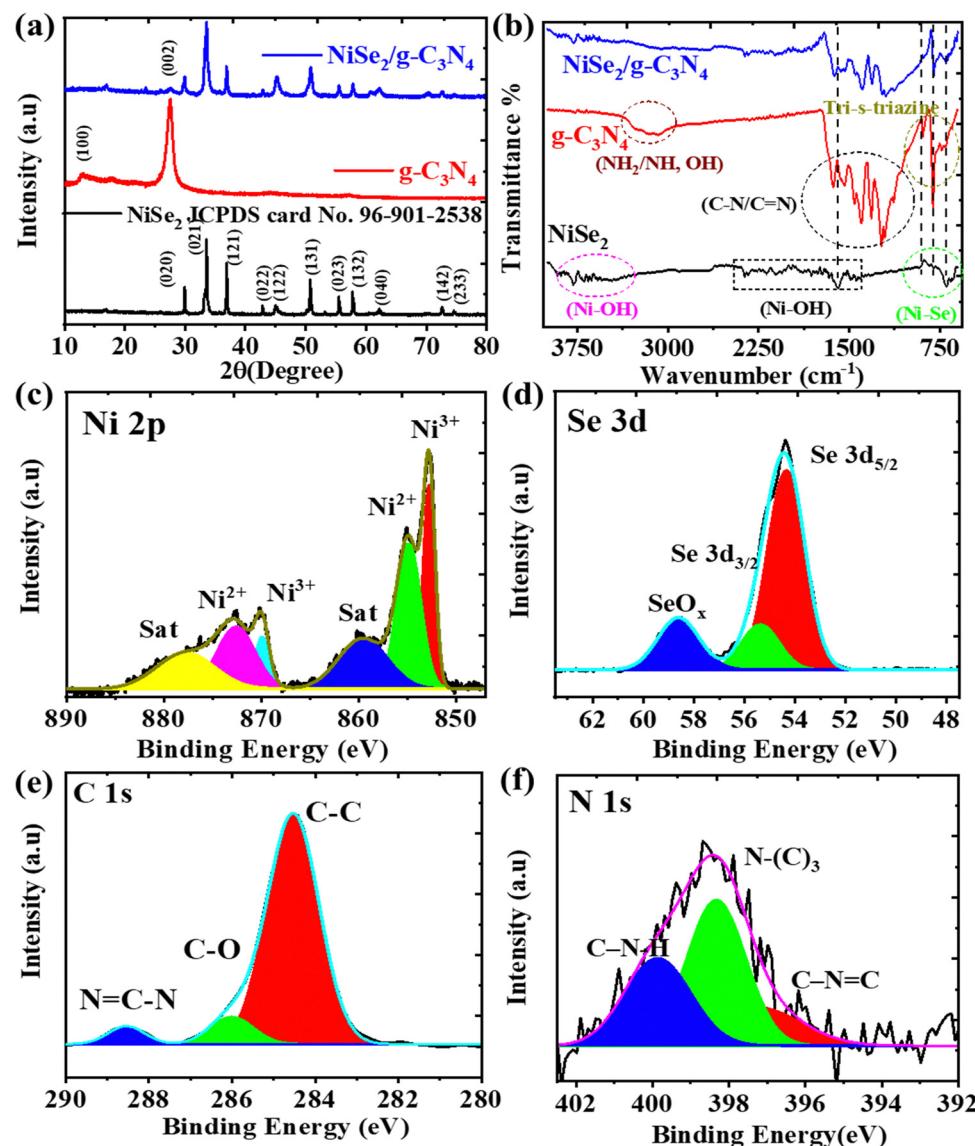


Fig. 1 (a) XRD and (b) FTIR patterns for the  $\text{NiSe}_2$ ,  $\text{g-C}_3\text{N}_4$ , and  $\text{NiSe}_2/\text{g-C}_3\text{N}_4$  nanocomposite. (c)–(f) XPS patterns of Ni 2p, Se 3d, C 1s, and N 1s in  $\text{NiSe}_2/\text{g-C}_3\text{N}_4$  nanocomposite.

growth. The favorable surface and electronic charge distribution of  $g\text{-C}_3\text{N}_4$  encourages the attachment of the  $\text{NiSe}_2$  nanoparticles on its surface. The directed attachment process, the Gibbs–Thompson law, and the Ostwald ripening stabilize the chemical system, forming the  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$  composite.<sup>35–38</sup>

### 3.2. Material characterization

The crystal phase and structure of  $\text{NiSe}_2$ ,  $g\text{-C}_3\text{N}_4$ , and  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$  were analyzed by X-ray diffraction (XRD). In the XRD pattern of  $g\text{-C}_3\text{N}_4$  (Fig. 1(a)), a peak at  $13.2^\circ$  is related to the (100) plane that arose due to in-planar tri-*s*-triazine units, whereas another peak at  $27.5^\circ$  belonged to the (002) plane originating from the layer stacking arrangement of conjugated aromatic systems.<sup>39</sup> The XRD pattern of  $\text{NiSe}_2$  reveals stronger intensity peaks at  $2\theta = 29.93^\circ$ ,  $33.55^\circ$ ,  $36.91^\circ$ ,  $50.71^\circ$ , and  $57.79^\circ$  corresponding to the crystal planes of (020), (021), (121), (131), and (132), respectively, which was confirmed from the standard card (JCPDS no. 96-901-2538).<sup>40</sup> The stronger peaks in the composite sample proved that the  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$  composite was successfully synthesized, and that there were no extra peaks. The peak positions of  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$  are consistent with  $\text{NiSe}_2$ , and a smaller peak of  $g\text{-C}_3\text{N}_4$  at  $27.5^\circ$  was observed suggesting that the crystal structure remains unaffected in presence of  $g\text{-C}_3\text{N}_4$ . Using the Debye Scherrer equation, the calculated crystallite sizes for  $\text{NiSe}_2$  and  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$  samples were 26.16 and 24.89 nm, respectively. Surface functionalities were studied using FTIR spectroscopy. The FTIR spectra of  $\text{NiSe}_2$ ,  $g\text{-C}_3\text{N}_4$ , and  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$ , are shown in Fig. 1(b). A peak

at  $801\text{ cm}^{-1}$  arose due to the characteristic absorption of the condensed heptazine heterocyclic ( $\text{C}_6\text{N}_7$ ) ring in  $g\text{-C}_3\text{N}_4$ . The bending and stretching modes of N-containing heterocycles in  $g\text{-C}_3\text{N}_4$  were characterized by the peak at  $890\text{ cm}^{-1}$  and the absorption band in the range of  $1000\text{--}1750\text{ cm}^{-1}$ , respectively. The broader peaks in  $3000\text{--}3500\text{ cm}^{-1}$  range were related to  $-\text{NH}$  or  $-\text{NH}_2$  groups in  $g\text{-C}_3\text{N}_4$ .<sup>41</sup> For  $\text{NiSe}_2$ , a broad band in the region of  $500$  to  $900\text{ cm}^{-1}$  is attributed to the stretching vibrations of nickel–selenium bonds. The bending and stretching vibrations of adsorbed water on  $\text{Ni}(\text{OH})_2$  are responsible for bands observed at around  $1600\text{ cm}^{-1}$  and  $3600\text{ cm}^{-1}$ , respectively. Moreover, the adsorption peaks of  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$  are comprised of the respective peaks of  $\text{NiSe}_2$  and  $g\text{-C}_3\text{N}_4$ , indicating the successful integration of the  $\text{NiSe}_2$  nanoparticles on the  $g\text{-C}_3\text{N}_4$  nanosheet.<sup>42–48</sup>

To investigate surface chemical states, XPS measurements were performed. Fig. S1a–c (ESI†) shows the XPS spectra of Ni 2p and Se 3d of  $\text{NiSe}_2$ . The Ni 2p spectrum contains Ni 2p1/2, Ni 2p3/2, and corresponding satellite peaks. The deconvoluted peaks of  $\text{Ni}^{2+}$  2p1/2 of  $\text{NiSe}_2$  and  $\text{Ni}^{2+}$  2p1/2 of  $\text{Ni}(\text{OH})_2$  are located at 870 and 872.77 eV, respectively.<sup>49</sup> The other two deconvoluted peaks at 852.82 and 855.17 eV are related to the  $\text{Ni}^{2+}$  2p3/2 of  $\text{NiSe}_2$  and  $\text{Ni}^{2+}$  2p3/2 of  $\text{Ni}(\text{OH})_2$ . The surface absorption of water may be responsible for the occurrence of the deconvoluted peaks of  $\text{Ni}^{2+}$  2p of  $\text{Ni}(\text{OH})_2$ .<sup>50</sup> The peaks at 860 and 880.15 eV correspond to standard Ni 2p satellite peaks.

Fig. S1d–f (ESI†) shows XPS survey spectra and the deconvolution curves for the  $g\text{-C}_3\text{N}_4$  sample. The C 1s XPS spectra

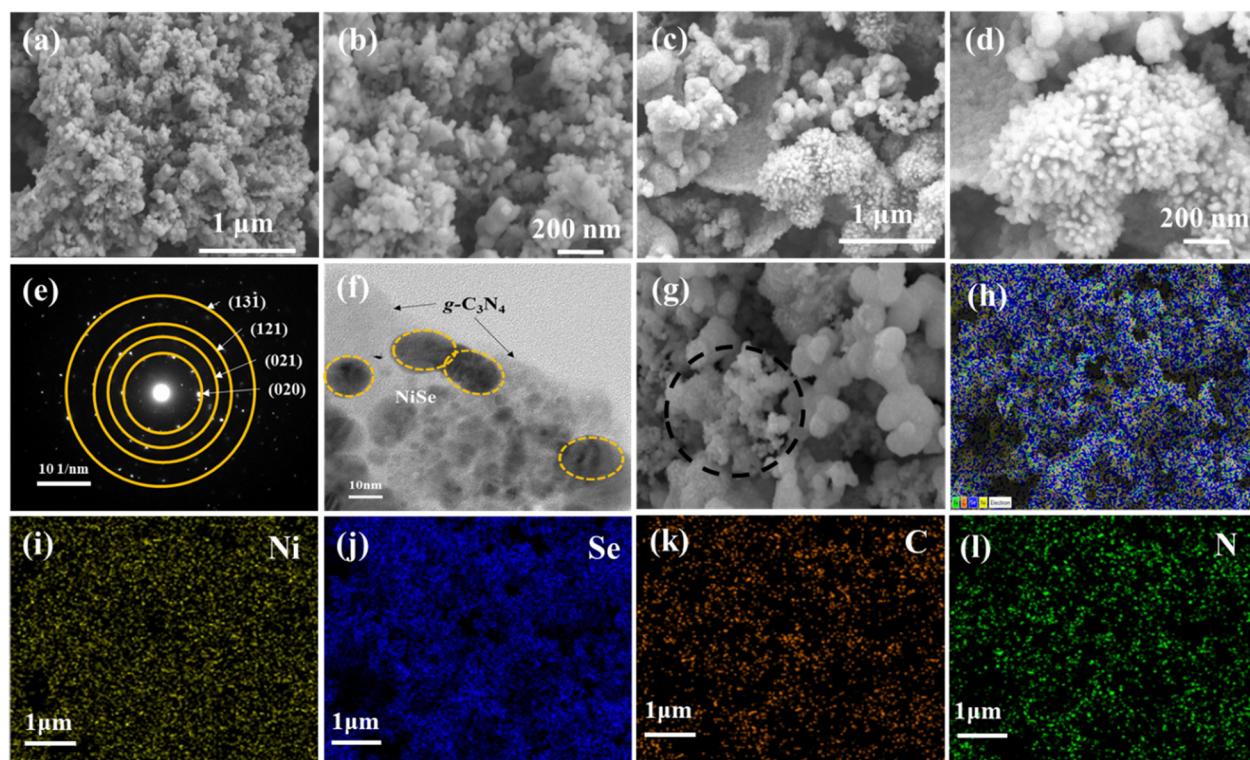


Fig. 2 FE-SEM images of (a), (b)  $\text{NiSe}_2$ , (c), (d)  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$ , and (e), (f) HR-TEM of  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$ . (g)–(l) Energy dispersive spectroscopy (EDS) mapping of elements Ni, Se, C, and O in  $\text{NiSe}_2/g\text{-C}_3\text{N}_4$ .



consist of three peaks at 287.33 eV (N=C=N), 285.51 eV (C=O) and 284.09 eV (C-C). For N 1s spectra, peaks are observed at 400.2 eV (-C-N-H), 399.07 eV (N-C<sub>3</sub>), and 397.8 eV (C-N=C). The presence of different functional groups consisting of C and N elements on the surface of the g-C<sub>3</sub>N<sub>4</sub> nanosheets could facilitate the ion adsorption and electron transfer required for the HER.<sup>21</sup> The XPS survey spectrum of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> (Fig. 1(c), (f) and Fig. S1g, ESI<sup>†</sup>), indicate the existence of Ni, Se, C, and N elements. In the case of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>, Ni 2p peaks are found to be red-shifted when compared to NiSe<sub>2</sub> implying that there was electron migration from g-C<sub>3</sub>N<sub>4</sub> to NiSe<sub>2</sub> and a subsequent charge redistribution around Ni atoms in the composite. This shows the greater synergy between NiSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> required for improved HER activity.

The growth and morphology of NiSe<sub>2</sub> on the g-C<sub>3</sub>N<sub>4</sub> sheets were analyzed by FE-SEM. Fig. 2(a)–(d) show the FE-SEM images of NiSe<sub>2</sub> and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>, respectively. The uniformly grown NiSe<sub>2</sub> nanoparticles on the g-C<sub>3</sub>N<sub>4</sub> nanosheets are seen. These particles are less agglomerated in NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> when compared to NiSe<sub>2</sub>. This leads to a greater availability of exposed active sites required for electrochemical reactions and ion adsorption during the HER. The structural analysis of the NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite was examined using HR-TEM, and it was clear from this that NiSe<sub>2</sub> grains were successfully grown on the g-C<sub>3</sub>N<sub>4</sub> nanosheets (Fig. 2(e) and (f)). This direct growth improves the mechanical and chemical stability needed for the increased electrocatalytic activity and stability, which in turn accelerates the ionic/electron transfer. The EDS spectrum of the NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite (Fig. 2(g)–(l)) indicates the presence of Ni, Se, C, and N elements in the NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite sample. All the elements show peaks at their known energies. The intensity count ratio for Ni and Se was approximately 1:2, which implied the presence of NiSe<sub>2</sub> in the composite. Fig. S1h (ESI<sup>†</sup>) displays the EDS elemental mapping for Ni, Se, C, and N in NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> samples. These images reveal the presence of all the elements in the composite, and a homogeneous distribution of NiSe<sub>2</sub> on the g-C<sub>3</sub>N<sub>4</sub> sheets could be inferred, confirming the successful fabrication of the nanocomposite.

The electrode/electrolyte compatibility is the most crucial for numerous issues that aid the HER performance. Thus,

surface wettability becomes significant for the analysis of electrode surface energy and transportation of charges/ions at the interface.<sup>51</sup> To do so, the contact angle, which determines the effective surface energy and hydrophilicity, is used to measure the interaction between electrode surfaces in contact with the electrolyte. The contact angle has an inverse relationship with the surface free energy. From Fig. 3(a), the contact angles of NF, g-C<sub>3</sub>N<sub>4</sub>/NF, NiSe<sub>2</sub>/NF, and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/NF for a 1 M KOH electrolyte are 0°, 113°, 64° and 36° respectively. Thus, the low contact angle of the NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> composite implies enhanced wettability.<sup>52,53</sup> The Fowkes' approximation was used to compute the surface free energy.<sup>54,55</sup> A set of four distinct standard liquids (distilled water, ethylene glycol, formamide, and glycerol) with known values of surface tension parameters (polar and dispersion components) were employed for this (see Fig. 3(b)).<sup>56</sup> The calculated surface free energies for g-C<sub>3</sub>N<sub>4</sub>/NF, NiSe<sub>2</sub>/NF, and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/NF were found to be 25.12, 38.49, and 49.2 mJ m<sup>-2</sup>, respectively (see Fig. 3(c)). The presence of lone pair electrons in g-C<sub>3</sub>N<sub>4</sub> enhanced the charge carrier mobility and wettability of the composite. As a result, the reduced contact angle and larger surface energy of the composite electrode aid in the enhancement of the interfacial charge transfer and ion diffusion accessibility.

### 3.3. Electrochemical studies

A three-electrode configuration was used to measure the HER electrochemical behavior of the synthesized samples. In a typical setup, NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/NF (working), Hg/HgO (reference), and graphite rod (counter) electrodes were used in 1.0 M KOH electrolyte. Further, a comparison was carried out with 20%Pt/C@NF and bare NF to study their HER activity. Fig. 4(a) displays iR-corrected LSV polarization curves measured in the potential range of -0.6 V to 0 vs. RHE. The overpotential values were found to be 228, 189, 153, 87, 116, and 64 mV for g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, NiSe<sub>2</sub>/10g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/30g-C<sub>3</sub>N<sub>4</sub> and 20%Pt/C electrodes, respectively, at a current density of 10 mA cm<sup>-2</sup>. The NiSe<sub>2</sub>-based samples demonstrated higher cathodic currents and more positive onset potentials compared to the bare NF indicating the greater HER activities of nickel selenides compared to that of Ni metal. Thus, the HER overpotential for

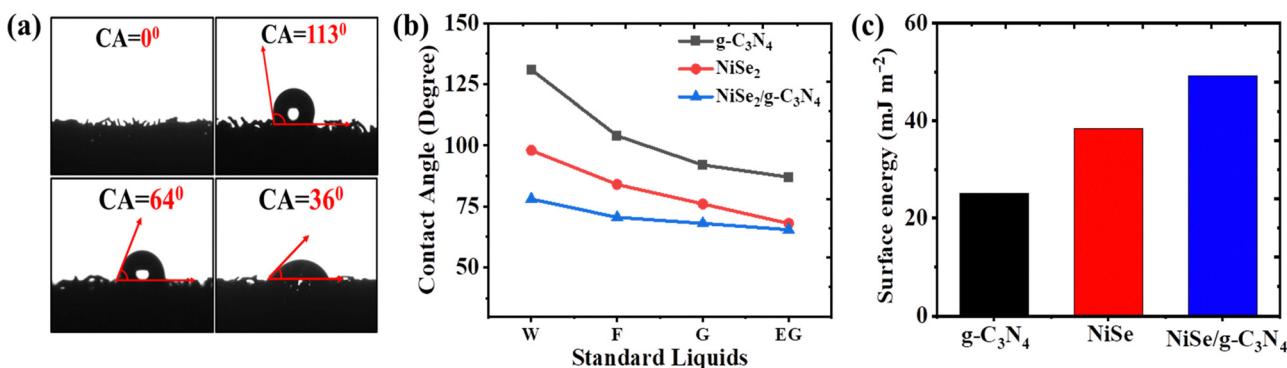


Fig. 3 (a) Contact angle of NF, g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> electrodes with 6 M KOH solution. (b) The contact angle of g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> electrodes with distilled water (W), ethylene glycol (EG), glycerol (G), formamide (F) as standard liquids. (c) Surface energy of g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> electrodes.



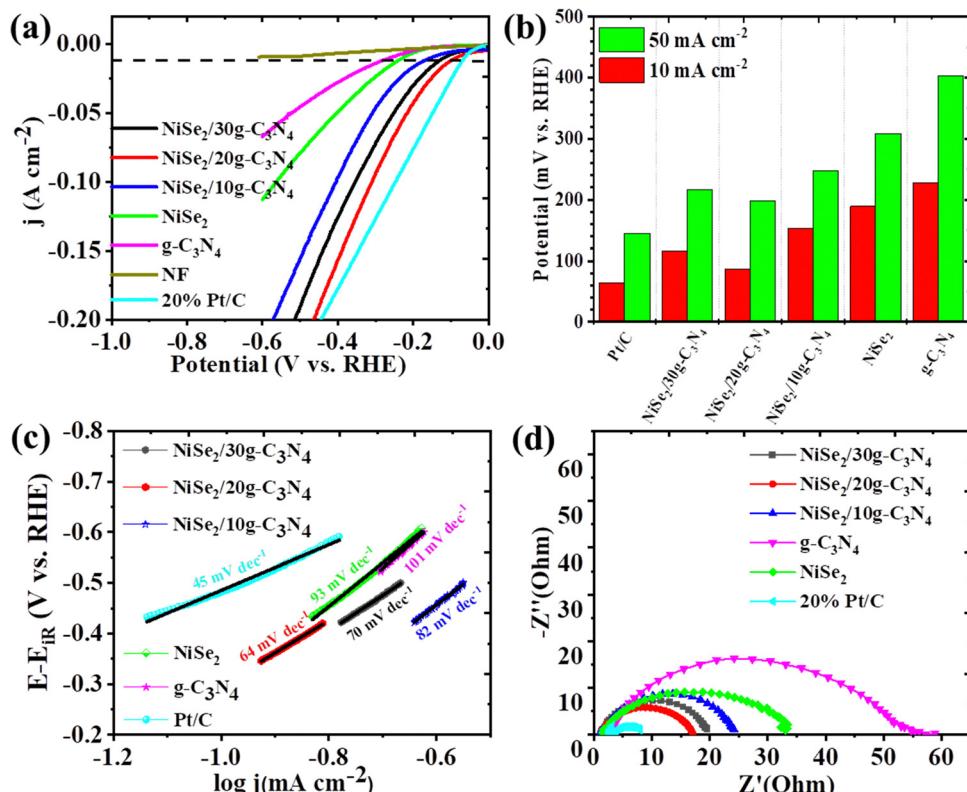


Fig. 4 HER performances (a) LSV, (b) overpotentials, (c) Tafel plots, and (d) Nyquist plot of NiSe<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/10g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/30g-C<sub>3</sub>N<sub>4</sub>, and 20%Pt/C.

NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> was just 23 mV more than Pt/C@NF and is the lowest among the prepared samples. Additionally, the overpotentials for all the samples were also measured and compared at a current density of 50 mA cm<sup>-2</sup> (see Fig. 4(b)). The increase in the current density, increases the overpotential value considerably. The sequence in the decreasing order for the overpotential is g-C<sub>3</sub>N<sub>4</sub> > NiSe<sub>2</sub> > NiSe<sub>2</sub>/10g-C<sub>3</sub>N<sub>4</sub> > NiSe<sub>2</sub>/30g-C<sub>3</sub>N<sub>4</sub> > NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub>, and 20%Pt/C. Thus, compared to the other samples, NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> exhibits the lowest overpotential and is closer to that of the 20%Pt/C electrode even at a high current density of 50 mA cm<sup>-2</sup>.

The Tafel slopes derived from related LSV sweeps aid in a better understanding of the HER reaction kinetics (Fig. 4(c)). The Tafel slopes for g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, NiSe<sub>2</sub>/10g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/30g-C<sub>3</sub>N<sub>4</sub> and 20% Pt/C were calculated to be 103, 93, 82, 64, 70, and 45 mV dec<sup>-1</sup>, respectively. Pt/C shows the lowest Tafel slope and best HER activity. However, NiSe<sub>2</sub>/20 g-C<sub>3</sub>N<sub>4</sub> shows a lower Tafel slope and an accelerated HER when compared to those of the other samples. The Volmer step serves as a bottleneck for the Volmer–Heyrovsky process in alkaline HER. Thus, heterostructured electrocatalysts with their electronic structure modulation and multiple active sites can promote the adsorption of H<sub>ad</sub>/OH<sub>ad</sub> for faster water dissociation in the Volmer step-determined alkaline HER phenomenon.<sup>57</sup> Moreover, the Tafel value is considerably lower than the theoretical Tafel slope of 120 mV dec<sup>-1</sup> for the Volmer step in alkaline HER, indicating an accelerated water dissociation for NiSe<sub>2</sub>/20

g-C<sub>3</sub>N<sub>4</sub>.<sup>49</sup> According to Tafel slope calculations, the synthesized electrocatalyst NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> follows the Volmer–Heyrovsky mechanism.

Taking into consideration the HER properties, *i.e.* overpotential and Tafel slope, a comparison of our work with that of different research groups, is shown in Table S1 (ESI†). The NiSe@g-C<sub>3</sub>N<sub>4</sub> electrode shows the lowest Tafel slope and overpotential amongst all the reported electrocatalysts, suggesting that there is superior HER electrocatalytic activity in an alkaline medium. This high HER catalytic activity of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> may correspond to the optimum charge transfer kinetics, intrinsic electrode activity, and the presence of several active sites.

EIS measurements help in examining the electrode kinetics. The Nyquist plot helps in the evaluation of  $R_s$  (solution resistance) and  $R_{ct}$  (charge transfer resistance). The magnitude of  $R_s$  is obtained from the X-intercept of the Nyquist curve, while  $R_{ct}$  is dependent on the diameter of the semi-circle.<sup>58</sup> The low value of  $R_s$  implies that there is better electrical integration of the electrode/electrolyte. From Fig. 4(d), it is seen that the diameter of the semi-circle for NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> is smaller than that of the other samples, which implies there is a lower  $R_{ct}$  at the electrode/electrolyte interface during the HER. The  $R_{ct}$  values of g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, NiSe<sub>2</sub>/10g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>/30g-C<sub>3</sub>N<sub>4</sub> and 20%Pt/C were calculated to be 55.34, 33.04, 24.17, 17.04, 19.59, and 7.93 Ω, respectively. Thus, NiSe@20g-C<sub>3</sub>N<sub>4</sub> shows higher charge transfer kinetics and HER activity compared to the other samples during alkaline water oxidation.



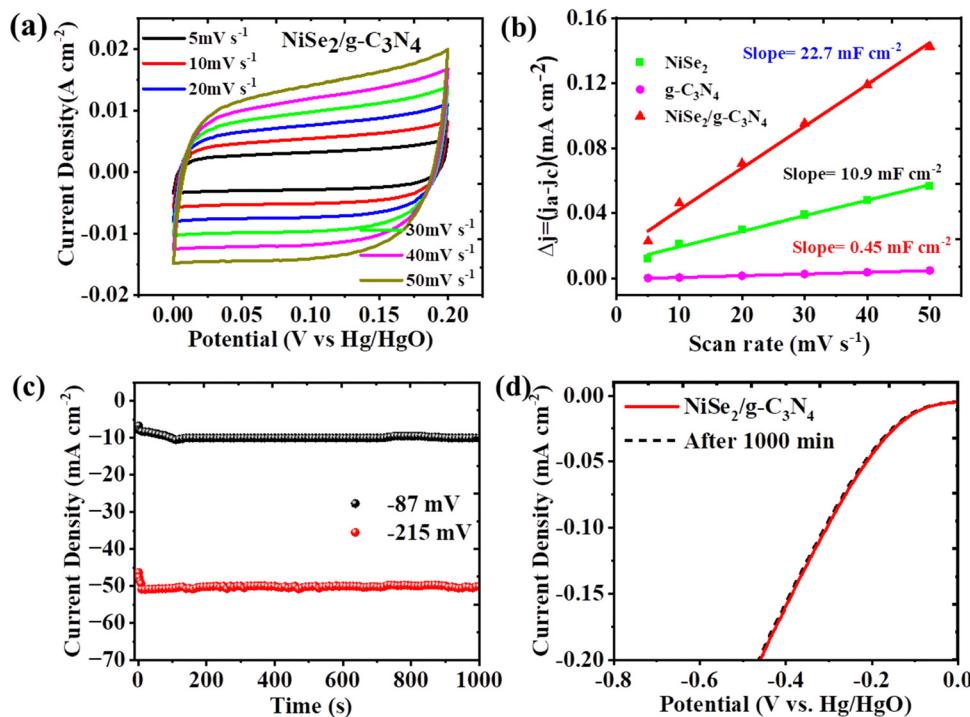


Fig. 5 (a) CV of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> at 5–50 mV s<sup>-1</sup> scan rates, (b) estimated values of  $C_{dl}$  for g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, and NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>. (c) Chronoamperometric measurement at constant potentials -0.087 and 0.215 V vs. RHE for NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>. (d) LSV curves of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> before and after 1000 min.

The electrochemical active surface area (ECSA) was determined using scan rate-dependent normalized CV-derived  $C_{dl}$  measurements in the non-faradaic region. The  $C_{dl}$  values for g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, and NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub>, were computed to be 6.45, 10.9 and 22.7 mF cm<sup>-2</sup>, respectively, (Fig. 5(a), (b), and Fig. S2b-d, ESI<sup>†</sup>). Thus, NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> displayed a  $C_{dl}$  which is greater than that of bare NiSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. Accordingly, the ECSA of g-C<sub>3</sub>N<sub>4</sub>, NiSe<sub>2</sub>, and NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> electrodes were calculated to be 161.25, 275.5, and 567.5 cm<sup>-2</sup>, respectively. It is also seen that the  $C_{dl}$  and ECSA values of NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> are higher than those of other samples. This implies that NiSe<sub>2</sub>@g-C<sub>3</sub>N<sub>4</sub> has the highest density of HER active sites. The turnover frequency (TOF) was calculated to study the intrinsic activity. The TOF values for NiSe<sub>2</sub>, and NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> were found to be 0.054 and 0.085 s<sup>-1</sup>, respectively. A TOF value of 0.085 s<sup>-1</sup> means that 85 hydrogen molecules are produced per second per active site.<sup>59</sup> Thus, the intrinsic activity for NiSe<sub>2</sub>/20g-C<sub>3</sub>N<sub>4</sub> was the highest among all the prepared samples.

For commercial scale-up of hydrogen production using water decomposition, in addition to high performance, the long-term stability also becomes significant. The chronoamperometry measurements were carried out for NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> electrode at two different potentials *i.e.* 87 and 215 mV vs. RHE for a time interval of 1000 min. Fig. 5(c) demonstrates that the current density fairly remains constant even after 1000 min of HER, which explains the long-term durability of the electrode. This stability is higher when compared to that of the bare NiSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> electrodes (see Fig. S2a, ESI<sup>†</sup>). Moreover, LSV curves did not change significantly even after 1000 min of the experiment (Fig. 5(d)), suggesting the potential of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>

for long-run applications. As a consequence, the enhanced electrocatalytic performance of NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> over bare NiSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> is the result of the modified surface chemistry generated by g-C<sub>3</sub>N<sub>4</sub> and tailored electronic characteristics of the composite. Thus, the optimal loading of 20g-C<sub>3</sub>N<sub>4</sub> in the NiSe<sub>2</sub> composite showed an enhanced synergistic interaction and provided a balance between active sites and electron transfer pathways, thus enhancing the charge transfer kinetics and HER activity. This loading also provided an optimal surface area, facilitating efficient mass/charge transport, while promoting a favorable electronic structure that optimized the adsorption and activation of hydrogen intermediates during the HER process.

## 4. Conclusion

In summary, the synthesis of a NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> nanocomposite using a simple hydrothermal technique was carried out. The composite electrode demonstrated high HER catalytic activity in 1 M KOH aqueous solution. The Tafel slope and overpotential values for NiSe<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> were less than those for the NiSe<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> electrodes. The nanocomposite shows excellent performance which is close to that of the Pt/C catalyst. Moreover, long term stability for 1000 min without performance decline was achieved. A stronger NiSe<sub>2</sub> catalyst supported by the g-C<sub>3</sub>N<sub>4</sub> interface arises primarily due to *in situ* growth and higher chemical stability. The electrochemical tests and analysis reveal that improved intrinsic catalytic activity, larger ECSA, lowered contact angle, and faster charge kinetics contribute to

the excellent catalytic performance. This study sheds light on the development of a high-performance, long-term stable, noble-metal-free electrocatalyst for use in the HER.

## Data availability

Data will be made available on request.

## Author contributions

Somnath R. Khaladkar: conceptualization, data curation, formal analysis, investigation, validation, visualization, writing – original draft. Oshnik Maurya: data curation, formal analysis, writing – original draft. Girish Gund: validation, visualization, writing – review and editing. Bhavesh Sinha: writing – review and editing. Girish Kamble: data curation. Jin Hyeok Kim: resources, project administration, supervision, funding acquisition. R. R. Deshmukh: project administration, resources, writing – review and editing. Archana Kalekar: conceptualization, funding acquisition, investigation, project administration, resources, supervision, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

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## References

- O. Maurya, S. R. Khaladkar, B. Sinha, B. M. Bhanage, R. R. Deshmukh, J. H. Kim and A. Kalekar, *Electrochim. Acta*, 2023, **471**, 143391.
- S. Lavate, H. P. S. Yalamati and R. Srivastava, in *Solar-Driven Green Hydrogen Generation and Storage*, ed. R. Srivastava, J. Chattopadhyay and D. M. F. Santos, Elsevier, 2023, pp.507–524.
- N. Kumar, M. Rehan, S. Khaladkar, O. Maurya, K. Rao, A. Kalekar, M. Kumar and J. Kumar, *Mater. Chem. Phys.*, 2024, **316**, 129072.
- O. Maurya, S. Khaladkar, M. R. Horn, B. Sinha, R. Deshmukh, H. Wang, T. Y. Kim, D. P. Dubal and A. Kalekar, *Small*, 2021, **17**, 1–29.
- S. Khaladkar, G. Gund, O. Maurya, B. Sinha, P. Salame, D. Dubal, R. Deshmukh and A. Kalekar, *Adv. Energy Sustainability Res.*, 2023, 2300013.
- J. B. M. Parambath, N. Hussain, H. Alawadhi, Y. Park, D. D. Dionysiou, C. Han and A. A. Mohamed, *Comments Inorg. Chem.*, 2022, **42**, 249–270.
- R. R. Deshmukh, A. S. Kalekar, S. R. Khaladkar and O. C. Maurya, in *Nanotechnology for Energy and Environmental Engineering*, ed. L. Ledwani and J. S. Sangwai, Springer International Publishing, Cham, 2020, pp.329–354.
- M. R. Ansari, S. Khaladkar, A. Kalekar, M.-D. Kim and K. R. Peta, *J. Energy Storage*, 2023, **74**, 109494.
- S. Shen, H. Zhang, K. Song, Z. Wang, T. Shang, A. Gao, Q. Zhang, L. Gu and W. Zhong, *Angew. Chem., Int. Ed.*, 2024, **63**, e202315340.
- X. Wang, Y. Fei, J. Chen, Y. Pan, W. Yuan, L. Y. Zhang, C. X. Guo and C. M. Li, *Small*, 2022, **18**, 2103866.
- X. Wang, Y. Fei, W. Wang, W. Yuan and C. M. Li, *ACS Appl. Energy Mater.*, 2019, **2**, 8851–8861.
- S. Bama Sundararaj, S. Tamilarasan, K. Kadirvelu and S. Thangavelu, *Appl. Surf. Sci.*, 2023, **612**, 155785.
- Z. Wang, Z. Lin, Y. Wang, S. Shen, Q. Zhang, J. Wang and W. Zhong, *Adv. Mater.*, 2023, **35**, 1–8.
- N. Sahu, J. K. Das and J. N. Behera, *Inorg. Chem.*, 2022, **61**, 2835–2845.
- W. Yuan, Y. Li, L. Liang, F. Wang and H. Liu, *ACS Appl. Energy Mater.*, 2022, **5**, 5036–5043.
- Z. Tian, Y. Liu, Q. Xu, Y. Shi, C. Ma, B. Peng, G. Liu, J. Yang and W. Zheng, *Electrochim. Acta*, 2022, **425**, 140711.
- K. Song, H. Zhang, Z. Lin, Z. Wang, L. Zhang, X. Shi, S. Shen, S. Chen and W. Zhong, *Adv. Funct. Mater.*, 2023, **2312672**, 1–9.
- X. Fan, X. Wang, W. Yuan and C. M. Li, *Sustainable Energy Fuels*, 2017, **1**, 2172–2180.
- Y. Chen, B. Zhang, Y. Liu, J. Chen, H. Pan and W. Sun, *Mater. Today Catal.*, 2023, **1**, 100003.
- S. R. Khaladkar, O. Maurya, G. Gund, B. Sinha, D. Dubal, R. R. Deshmukh and A. Kalekar, *J. Energy Chem.*, 2023, **87**, 304–313.
- K. Li, Z. Shi, L. Wang, W. Wang, Y. Y. Liu, H. Cheng, Y. Yang and L. Zhang, *J. Hazard. Mater.*, 2023, **448**, 130890.
- S. R. Khaladkar, O. Maurya, G. Gund, B. Sinha, D. Dubal, R. Deshmukh and A. Kalekar, *ACS Appl. Mater. Interfaces*, 2024, **16**(9), 11408–11420.
- M. Guan, C. Wang, S. Li, H. Du and Y. Yuan, *ACS Sustainable Chem. Eng.*, 2020, **8**, 10313–10320.
- M. Zulqarnain, A. Shah, M. A. Khan, F. Jan Iftikhar and J. Nisar, *Sci. Rep.*, 2020, **10**, 1–8.
- S. Yousefzadeh and N. Morovati, *Int. J. Hydrogen Energy*, 2020, **45**, 33512–33520.
- X. Lv, W. Wei, H. Wang, B. Huang and Y. Dai, *Appl. Catal., B*, 2020, **264**, 118521.
- J. Jia, W. Sun, Q. Zhang, X. Zhang, X. Hu, E. Liu and J. Fan, *Appl. Catal., B*, 2020, **261**, 118249.



- 28 Z. Zhuang, Y. Li, Z. Li, F. Lv, Z. Lang, K. Zhao, L. Zhou, L. Moskaleva, S. Guo and L. Mai, *Angew. Chem., Int. Ed.*, 2018, **57**, 496–500.
- 29 H. Jin, X. Liu, Y. Jiao, A. Vasileff, Y. Zheng and S. Z. Qiao, *Nano Energy*, 2018, **53**, 690–697.
- 30 J. Liang, Y. Zheng, J. Chen, J. Liu, D. Hulicova-Jurcakova, M. Jaroniec and S. Z. Qiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 3892–3896.
- 31 R. Shwetharani, S. Kapse, R. Thapa, D. H. Nagaraju and R. G. Balakrishna, *ACS Appl. Energy Mater.*, 2020, **3**, 12682–12691.
- 32 G. Dong, H. Fan, K. Fu, L. Ma, S. Zhang, M. Zhang, J. Ma and W. Wang, *Composites, Part B*, 2019, **162**, 369–377.
- 33 Y. Liu, Y. Zheng, Q. Xu, Y. Shi, Z. Tian, R. Wang, G. Zhang, J. Chen, Z. Wang and W. Zheng, *Chem. Eng. J.*, 2020, **387**, 124121.
- 34 Z. Chen, Y. Gao, F. Chen and H. Shi, *Chem. Eng. J.*, 2021, **413**, 127474.
- 35 H. Cölfen and S. Mann, *Angew. Chem., Int. Ed.*, 2003, **42**, 2350–2365.
- 36 B. Z. Zhang, H. Sun, X. Shao, D. Li, H. Yu and M. Han, *Adv. Mater.*, 2005, **17**, 42–47.
- 37 X. Wang, W. Mao, J. Zhang, Y. Han, C. Quan, Q. Zhang, T. Yang, J. Yang, X. Li and W. Huang, *J. Colloid Interface Sci.*, 2015, **448**, 17–23.
- 38 J. Safaei, N. A. Mohamed, M. F. Mohamad Noh, M. F. Soh, N. A. Ludin, M. A. Ibrahim, W. N. Roslam Wan Isahak and M. A. Mat Teridi, *J. Mater. Chem. A*, 2018, **6**, 22346–22380.
- 39 J. Kavil, P. M. Anjana, P. Periyat and R. B. Rakhi, *Sustainable Energy Fuels*, 2018, **2**, 2244–2251.
- 40 G. K. Subhash, M. D. Benoy, J. Duraimurugan, S. Prabhu, R. Siranjeevi, R. Ramesh, G. Suresh Kumar and M. Shkir, *Inorg. Chem. Commun.*, 2022, **142**, 109719.
- 41 F. Shiravani, J. Tashkhourian and B. Haghghi, *Sustainable Energy Fuels*, 2021, **5**, 3229–3239.
- 42 T. Ivanova, A. Harizanova, M. Shipochka and P. Vitanov, *Materials*, 2022, **15**, 1742.
- 43 S. Wang, P. He, L. Jia, M. He, T. Zhang, F. Dong, M. Liu, H. Liu, Y. Zhang, C. Li, J. Gao and L. Bian, *Appl. Catal., B*, 2019, **243**, 463–469.
- 44 D. Sun, J. Zhang, H. Ren, Z. Cui and D. Sun, *J. Phys. Chem. C*, 2010, **114**, 12110–12116.
- 45 J. Nai, X. Xu, Q. Xie, G. Lu, Y. Wang, D. Luan, X. Tao and X. W. Lou, *Adv. Mater.*, 2022, **34**, 1–7.
- 46 B. Jansi Rani, G. Ravi, R. Yuvakkumar, B. Saravanakumar, M. Thambidurai, C. Dang and D. Velauthapillai, *ACS Omega*, 2020, **5**, 14702–14710.
- 47 S. Manickam, H. Kuzhandaivel, Y. Selvaraj, M. C. Franklin and K. Sivalingam Nallathambi, *Dalton Trans.*, 2022, **51**, 1542–1552.
- 48 I. Ahmad, S. B. Khan, T. Kamal and A. M. Asiri, *J. Mol. Liq.*, 2017, **229**, 429–435.
- 49 Y. Bai, H. Zhang, X. Lu, L. Wang, Y. Zou, J. Miao, M. Qiao, Y. Tang and D. Zhu, *Chem. – Eur. J.*, 2023, **29**(28), 0947–6539, DOI: [10.1002/chem.202300205](https://doi.org/10.1002/chem.202300205).
- 50 L. Zhao, Y. Zhang, Z. Zhao, Q. H. Zhang, L. B. Huang, L. Gu, G. Lu, J. S. Hu and L. J. Wan, *Natl. Sci. Rev.*, 2020, **7**, 27–36.
- 51 M. M. Vadiyar, S. C. Bhise, S. K. Patil, S. S. Kolekar, A. R. Shelke, N. G. Deshpande, J. Y. Chang, K. S. Ghule and A. V. Ghule, *Chem. Commun.*, 2016, **52**, 2557–2560.
- 52 H. S. Lee, G. S. Gund and H. S. Park, *J. Power Sources*, 2020, **451**, 227763.
- 53 T. Liu, K. Wang, Y. Chen, S. Zhao and Y. Han, *Green Energy Environ.*, 2019, **4**, 171–179.
- 54 F. M. Fowkes, *J. Phys. Chem.*, 1963, **67**, 2538–2541.
- 55 F. M. Fowkes, *J. Adhes. Sci. Technol.*, 1987, **1**, 7–27.
- 56 R. R. Deshmukh and A. R. Shetty, *J. Appl. Polym. Sci.*, 2008, **107**, 3707–3717.
- 57 X. Ma, J. Yang, X. Xu, H. Yang and C. Peng, *RSC Adv.*, 2021, **11**, 34432–34439.
- 58 N. O. Laschuk, E. B. Easton and O. V. Zenkina, *RSC Adv.*, 2021, **11**, 27925–27936.
- 59 K. S. Ranjith, S. Y. Lee, S. M. Ghoreishian, N. R. Chodankar, G. S. Rama Raju, S. J. Patil, Y. S. Huh, S. J. Park and Y. K. Han, *Carbon N. Y.*, 2023, **206**, 246–259.

