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In situ-Electrochemically reduced graphene oxide integrated with cross-linked supramolecular polymeric network for electrocatalytic hydrogen evaluation reaction

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ABSTRACT

Herein, we report the synthesis of a new supramolecular polymeric network (**PCN**) assembled through crosslinking of propyl bromide substituted tetraphenyl porphyrin with perhydroxy-cucurbit [8]uril and its use in the electrocatalytic hydrogen evaluation reaction after loading with nickel and integrating with *in situ*-electrochemically reduced graphene oxide (**ERGO**). Electrode was prepared by first coating graphene oxide on the FTO substrate followed by layering the nickel loaded **PCN** and finally by applying an appropriate voltage to reduce the graphene oxide *in situ* electrochemical reaction. The loading of nickel cocatalyst into **PCN** together with the integration of **ERGO** layer substantially improved its HER efficiency. Effect of various concentrations of Ni and **GO** on the HER activity of the developed electrocatalyst were investigated. Therein, **ERGO**₁/Ni₂@**PCN** catalyst containing 41% Ni and 50% **GO** (with respect to **PCN**) with only one layer of each component demonstrated excellent HER activity and stability with low onset and overpotentials of -20 mV, $\eta@10$ mA cm⁻² of -360 mV, respectively, and remarkable hydrogen generation rate of 27.5 mmol h⁻¹ g⁻¹ in 1 M KOH. This noble-metal-free catalytic system is simple yet highly promising for the efficient hydrogen evolution reaction from water splitting.

1. Introduction

Hydrogen is considered as a promising alternative to substitute conventional fossil fuels due to its high energy density, renewability, sustainability, environmental safety and cleanliness [1,2]. Electrocatalytic hydrogen evolution reaction (HER) has been widely regarded as an efficient approach to produce hydrogen from water splitting. In this context, HER catalytic systems require efficient catalysts to promote the sluggish kinetics for hydrogen production [3,4], where low-cost and stability of the catalysts are two essential factors.

Recently, porphyrin derivatives have attracted growing interest as organic building blocks of HER catalytic systems owing to their synthetic versatility, chemical stability, redox behavior and quite unique physicochemical properties [4–6]. Because of their eighteen delocalized π -electrons, porphyrins exhibit remarkable photo- and electrochemical properties. Besides, the unique structural features of these aromatic platforms facilitate the attachment of various functionalities to their

large hydrophobic cores, resulting in multifunctional structures with the desired properties and functions that have been largely explored in several frontline applications [7–13]. To date various porphyrin-based assemblies such as self-assembled porphyrin nanostructures [14–17], porphyrin-based imine gels [5], metalloporphyrins [15,17–19], and porphyrin-based metal-free covalent organic polymer [20] have been served as efficient HER catalysts for electrocatalytic hydrogen generation from water splitting.

Owing to their unique properties, porphyrins have been widely used in the construction of supramolecular architectures with cucurbit [n] urils (**CB** [5–8]) [21–23]. **CB** [n]s are highly appealing macrocycles with a rigid symmetrical structure that have two identical carbonyl-rimmed portals and a hydrophobic cavity. They can be found in numerous sizes depending on the number of glycol units present in their structure, cucurbit [8]uril (**CB** [8]) for instance, contains eight glycol units and has a largest cavity size among the other homologues. Their impressive structural features together with exceptional binding ability,

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non-toxicity, and high biocompatibility, thermal and chemical stability make **CB** [n]s as fascinating building blocks for the construction of supramolecular architectures with diverse applications [24–30]. However, the difficulty of direct functionalization of **CB** [n] has restricted the studies on the functionalized CB-based supramolecular assemblies [26, 27,31]. Herein, the development of multifunctional supramolecular assemblies based on covalent conjugation of functionalized **CB** [n]s to porphyrin cores is the subject of great importance to achieve well-ordered structures with diverse applications. In this context, the first examples of the covalent **CB** [n]-porphyrin conjugations have recently been reported by our group, where the developed assemblies were successfully utilized in photodynamic antibacterial therapy and cancer therapy as well as photo/electrocatalytic hydrogen generation from water splitting [32–38].

Graphene, a one-atom thick two-dimensional sheets of sp² hvbridized carbon atoms arranged in honeycomb lattice, has dramatically shaped queries in many fields particularly as HER catalysts due to its unique electrical, thermal, mechanical, and optical properties together with large surface area [39–41]. Owing to its high thermal conductivity, graphene attains good charge carrier mobility at room temperature [42]. Moreover, graphene is a powerful electron acceptor that improves induced charge transfer and prevents the reverse reaction by separating the evolution sites of hydrogen and oxygen thus resulting in an enhanced hydrogen production efficiency [43]. Among different techniques to produce graphene [44,45], chemical reduction of graphene oxide (GO) is believed to be the most efficacious method with respect to its low cost and significant scalability [46]. Electrochemically reduced graphene oxide (ERGO) is found to be much more conductive while possessing a lower oxygen to carbon ratio than the conventional chemically reduced one [47]. The electrochemical reduction of GO is achieved by applying a negative potential that reduces the oxygen functional groups on its surface [48,49].

Over the past decade, a series of graphene-porphyrin composites have been synthesized to use in various applications such as electrochemical biosensing [50], solar light harvesting [51], photothermal therapy of brain cancer [52], electrocatalysis [53] and more recently as efficient catalysts to produce hydrogen from water splitting [54–57].

The encouraging results of all the mentioned above studies motivated us to develop a new HER electrocatalyst based on cross-linked porphyrin-CB [8] network in combination with electrochemically reduced graphene oxide (ERGO). For this purpose, first perhydroxy CB [8] (CB8(OH)_n) was synthesized and then it was covalently attached to a suitably substituted tetraphenyl porphyrin core through Williamson ether reaction to produce PCN. The working electrode was then fabricated by layer by layer (LBL) coating of thin films of GO and Ni@PCN, respectively, over FTO followed by an electrochemical reduction procedure. The layer by layer technique has been applied in many research areas to construct multilayer nanocomposite thin films that have improved properties. It is a simple method based on the electrostatic interactions between oppositely charged monolayers on a solid support [58]. Nowadays, much attention shifted to the development of cost-effective electrocatalysts with non-precious metals such as Ni, Co and Fe [59]. The special 3d electronic distribution of Ni has given rise to considerable application of Ni-based catalysts toward hydrogen production especially in the alkaline medium [60]. Effect of different Ni and GO contents on the HER activity of the electrocatalyst was investigated and optimized. The developed ERGO1/Ni2@PCN catalyst demonstrated excellent HER activity and stability in alkaline media without any sacrificial agent.

2. Experimental section

2.1. Chemicals

4-methoxy benzaldehyde, pyrrole, trimethylamine, boron trifluoride diethyl ether, tetrachloro-1,4-benzoquinone, boron tribromide, 1,3-

dibromopropane, potassium carbonate, potassium persulfate, potassium sulfate, sodium hydride, graphite powder, potassium permanganate, hydrogen peroxide, phosphoric acid, sulfuric acid, hydrochloric acid, dimethyl sulfoxide, chloroform, methanol, and all the other chemicals and reagents used for synthesis procedures were of analytical grade and purchased from Sigma-Aldrich, unless otherwise stated. The deuterated solvents CDCl₃-*d1* and DMSO-*d*₆ were obtained from Merck and used in NMR. Nickel acetate tetra hydrate, potassium hydroxide, phosphate-buffered saline (PBS) and platinum on carbon (Pt/C), used in electrochemical experiments were obtained from Sigma-Aldrich. Nafion (5% w/w in water and 1-propanol) was purchased from Alfa Aesar and used as a binder during the electrode fabrication. Ultra-pure deionized water (R \geq 18 M Ω cm⁻¹) from Milli-Q plus water purification system (Millipore, Bedford, MA, USA) was used throughout the study.

2.2. Characterization methods

Mass spectra were recorded on Agilent 6210 LC/MS TOF mass spectrometer. ¹H NMR (proton nuclear magnetic resonance) spectra were acquired at 400 MHz using Bruker Avance III 400 MHz NMR spectrometer. Scanning electron microscopy (SEM) imaging and energy dispersive X-ray (EDX) analysis were obtained using FEI Technai G2 F30 SEM. Transmission electron microscopy (TEM) imaging was done by FEI Tecnai G2 F30 TEM. A Bruker Alpha-II Platinum ATR Fourier-transform infrared (FT-IR) spectrometer was used in this work. X-ray diffraction patterns were recorded by the X-ray diffractometer (XRD, X' pert pro MPD, PANalytical Empyrean) using Cu Kα irradiation source (40 kV, 45 mA, $\lambda = 1.5418$ Å). Raman spectra were recorded by a confocal Raman microscope (WITec Alpha 300R) from 500 to 3000 cm^{-1} , at an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) study was performed in a Thermo Fisher Scientific spectrometer. High resolution spectra were taken at fixed pass energy of 30 eV, spot size of \sim 400 µm and step size of 0.1 eV. Thermal stability of the sample was examined on TA Instruments Q500 thermogravimetric analyzer.

2.3. Synthesis and characterization of organic precursors

5,10,15,20-tetrakis (4-methoxyphenyl) porphyrin **TPP-4(OCH₃)**, 5,10,15,20-tetrakis (4-hydroxyphenyl)porphyrin (**TPP-4OH**) and **CB** [8] were synthesized according to the literature procedures [37,61,62].

2.3.1. Synthesis of perhydroxy-CB [8], CB8(OH)_n

CB8(OH)_n was synthesized modifying the reported procedure [31]. To a solution **CB** [8] (1.00 g, 0.75 mmol) in 50 mL degassed deionized water, K₂S₂O₈ (2.85 g, 10.5 mmol) and K₂SO₄ (1.84 g, 10.5 mmol) were added. The reaction mixture underwent 3 freeze-thaw cycles and then refluxed at 85 °C for 12 h, under nitrogen atmosphere. After cooling down to RT, the solid precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The obtained white solid was dissolved in DMSO and filtered. The filtrate was added dropwise into acetone and white solid was precipitated out, collected by filtration, washed with acetone and oven dried to give 920 mg CB8(OH)_n as white powder. Yield: 78%

ESI-MS (m/z): calcd. for C₄₈H₄₈O₁₇N₃₂Na [M1+Na]⁺: 1367.3774, Found: 1367.6933; calcd. for C₄₈H₄₈O₁₈N₃₂Na [M2+Na]⁺: 1383.3723, Found: 1383.6983; calcd. for C₄₈H₄₈O₁₉N₃₂H [M3+H]⁺: 1377.3853, Found: 1377.7019; calcd. for C₄₈H₄₈O₂₀N₃₂ [M4]: 1392.3724, Found: 1392.6995; calcd. for C₄₈H₄₈O₂₁N₃₂Na [M5+Na]⁺: 1431.3571, Found: 1431.7143; calcd. for C₄₈H₄₈O₂₂N₃₂K [M6+K]⁺: 1447.3519, Found: 1447.7430; calcd. for C₄₈H₄₈O₂₃N₃₂Na [M7+Na]⁺: 1463.3469, Found: 1463.7587; calcd. for C₄₈H₄₈O₂₄N₃₂Na [M8+Na]⁺: 1479.3418, Found: 1479.7884; calcd. for C₄₈H₄₈O₂₉N₃₂K [M1+Na]⁺: 1575.2904, Found: 1495.7793; calcd. for C₄₈H₄₈O₃₀N₃₂K [M13+K]⁺: 1591.48528, Found: 1591.8169; calcd. for C₄₈H₄₈O₃₁N₃₂Na [M15+Na]⁺: 1591.5063, Found: 1591.8169; calcd. for C₄₈H₄₈O₃₂N₃₂ 1584.8246; calcd. for $C_{48}H_{48}O_{32}N_{32}H [M16+H]^+:1585.5192$, Found: 1585.8160; calcd. for $C_{48}H_{48}O_{32}N_{32}K_2 [M16+2K]^{2+}: 831.1194$, Found: 831.4815; calcd. for $C_{48}H_{48}O_{30}N_{32}K_2 [M14+2K]^{2+}: 815.3245$, Found: 815.6512; calcd. for $C_{48}H_{48}O_{32}N_{32}N_{32} [M16+2Na]^{2+}: 815.251$, Found: 815.6512; calcd. for $C_{48}H_{48}O_{29}N_{32}H_2 [M13+2H]^{2+}: 769.2711$, Found: 796.4717; calcd. for $C_{48}H_{48}O_{26}N_{32}H_2 [M11+2H]^{2+}: 753.2723$, Found: 753.4946; calcd. for $C_{48}H_{48}O_{26}N_{32}H_2 [M10+2H]^{2+}: 745.2748$, Found:745.4176; calcd. for $C_{48}H_{48}O_{25}N_{32}Na_2 [M9+2Na]^{2+}: 759.2683$, Found: 859.4134; calcd. for $C_{48}H_{48}O_{23}N_{32}Na_2 [M7+2Na]^{2+}: 729.2838$, Found: 729.4104; calcd. for $C_{48}H_{48}O_{23}N_{32}Na_2 [M7+2Na]^{2+}: 735.1959$, Found: 735.3826; calcd. for $C_{48}H_{48}O_{21}N_{32}Na_2 [M5+2Na]^{2+}: 727.2785$, Found: 735.4416; calcd. for $C_{48}H_{48}O_{20}N_{32}Na_2 [M5+2Na]^{2+}: 719.2810$, Found: 719.3795; calcd. for $C_{48}H_{48}O_{19}N_{32}K_2 [M3+2K]^{2+}: 737.2706$, Found: 727.4416; Where M is **CB8(OH)** and n is the number of hydroxy groups, $M_n \sim$ **CB8(OH)**_n.

2.3.2. Synthesis of TPP-4(OC₃H₆Br)

To a stirred solution of **TPP-4OH** (200 mg, 0.294 mmol) in DMF (5 mL), K_2CO_3 (325 mg, 2.35 mmol) was added under nitrogen atmosphere. The solution was stirred at RT for 1 h followed by adding 1,3-dibromopropane (0.42 mL, 4.20 mmol). The reaction mixture was stirred at RT for 72 h and the progress of the reaction was monitored with ESI-MS. After the reaction was over, the flask content was partitioned between chloroform/water ($450 \times mL$) using ice-cold water. The combined organic phase was dried over anhydrous MgSO₄ and evaporated *in vacuo* to give **TPP-4(OC₃H₆Br)** as purple solid. Yield: 280 mg, 82%.

ESI-MS (m/z): Calcd. for C₅₆H₅₀Br₄N₄O₄H [M+H]⁺: 1163.0603, Found: 1163.0762, Where M is **TPP-4(OC₃H₆Br**).

2.4. Synthesis of PCN

To a stirred solution of **CB8(OH)**_n (200 mg, 0.131 mmol) in 4 mL DMSO, NaH (50.4 mg, 2.10 mmol) was added under nitrogen atmosphere. After 1h stirring at RT, a solution of **TPP-4(OC**₃**H**₆**Br**) (152 mg, 0.131 mmol) in 2 mL DMSO was added into the flask and the reaction mixture was stirred at RT for 72 h. The flask content was then added dropwise into 15 mL deionized water, black solid was precipitated out, filtered, washed several times with water and chloroform to remove the unreacted precursors and finally vacuum-dried at 60 °C to obtain **PCN** as dark brown solid. Yield: 260 mg.

2.5. Synthesis of graphene oxide (GO)

The **GO** was obtained via exfoliation of graphite oxide. Graphite oxide was prepared by improved Hummers' method (Tour's method) through the oxidation of graphite powder [63]. Typically, 3 g graphite powder was added to a 9:1 (v/v) mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) under stirring. 18 g KMnO₄ was gradually added to the stirred suspension. The reaction mixture was further heated to 50 °C and stirred for 12 h. After cooling down to room temperature, the reaction mixture was poured into 400 mL ice and 3 mL H_2O_2 (30%). The resulting yellowish-brown product was centrifuged at 6000 rpm for 4 h in 10 min intervals and the supernatant was decanted away. The residue was then washed consecutively with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. The final solid was oven-dried at 60 °C for overnight to give graphite oxide flakes that were finely ground to obtain a fine dark-brown powder which was then dispersed in water and ultrasonicated for an hour to form stable suspensions of **GO**.

2.6. Electrochemical measurements

All electrochemical experiments were carried out using CHI-670 potentiostat (CH Instruments, China) with standard three-electrode quartz cell at room temperature. The catalyst modified fluorine tin oxide (FTO), platinum spiral wire and Ag/AgCl/KCl_(sat.) were used as the

working, counter and reference electrodes, respectively. The electrochemical experiments were performed in 0.1 M and 1 M KOH electrolytes. Prior to electrochemical analysis, the electrolyte system was purged with Argon gas (99.99% of purity) for 30 min to remove any dissolved gas in the electrolyte. Strips of 10×20 mm of 2 mm thick FTO glass were cut from a sheet obtained from Sigma-Aldrich. FTO substrates were cleaned by sequential sonication in water and isopropanol for 15 min and dried in air. The FTO surface was then activated at 450 °C for 2 h. Linear sweep voltammetry (LSV) measurements were conducted in Ar-saturated electrolyte at a scan rate of 10 mVs⁻¹. All potential values obtained (vs. Ag| AgCl| KCl(sat.)) were corrected to a reversible hydrogen electrode (RHE) using Nernst equation. Electrochemical impedance spectroscopy (EIS) measurements were obtained at -0.6 V (vs RHE) using the CHI-670 potentiostat. An ac signal amplitude of 5 mV was applied from 0.1 Hz to 100 kHz.

2.7. Preparation of ERGO/Ni@PCN coated FTO electrodes

At first, Ni@PCN ink was prepared by grinding nickel acetate tetrahydrate salt with PCN in certain weight ratios followed by mixing of the resulting composite with ethanol, water and Nafion for over-night. GO ink was then prepared by sonicating a known amount of graphite oxide powder in water and ethanol for 1 h. The catalyst modified FTO was achieved by LBL coating of GO and Ni@PCN layers, respectively, over the conductive side of FTO glass (2 \times 1 cm²) covering 1 \times 1 cm² area: first, a layer of 10 µl GO ink was coated over FTO with 10 µl Nafion by drop casting method and after drying under ambient conditions, 10 µl of Ni@PCN ink was drop casted as the second layer. These working electrodes were eventually dried at 60 °C for 1 h to obtain a consistent hybrid film of GO/Ni@PCN over FTO (see ESI for more details on electrode fabrication procedure). Once the hybrid thin film with desired ratio was fabricated on FTO, the corresponding GO/Ni@PCN complex was electrochemically reduced by cyclic voltammetry in Ar-saturated 0.1 M PBS (pH 7.4) to enhance its electrocatalytic HER activity. The system was swept between 0.0 and -1.5 V (vs Ag/AgCl) at 50 mV s⁻¹ for 50 cycles to achieve Ni@PCN functionalized electrochemically reduced graphene oxide (ERGO/Ni@PCN) thin film. Five different electrodes were prepared by varying nickel and graphene oxide concentrations: ERGO_{0.5}/Ni₂@PCN, ERGO₂/Ni₂@PCN, ERGO₁/Ni₂@PCN, ERGO₁/ Ni1@PCN and ERGO1/Ni0.5@PCN. The subscripts represent the weight ratios of nickel acetate salt and graphene oxide with respect to PCN.

3. Results and discussion

3.1. Synthesis and characterization of PCN

Scheme 1 represents the synthetic routes of precursors and the designed PCN. CB [8] and TPP-4(OCH₃) were synthesized as reported previously [37]. Hydroxylation of CB [8] with excess K_2SO_4 and K_2SO_8 afforded CB8(OH)_n [31]. TPP-4OH was synthesized through demethylation of methoxy groups of TPP-4(OCH₃) using borontribromide [37]. TPP-4(OC₃H₆Br), as the main porphyrin core, was finally synthesized by Williamson ether reaction of TPP-4OH in the presence of excess K_2CO_3 and 1,3-dibromopropane. CB8(OH)_n and TPP-4(OC₃H₆Br) were fully characterized by spectroscopic techniques (¹H NMR, FT-IR ESI-mass) (Figs. S1–S12).

With $CB(OH)_n$ and $TPP-4(OC_3H_6Br)$ in hand, we next set out to synthesize the target PCN through Williamson ether reaction of CB8 (OH)_n (1 equiv.) with $TPP-4(OC_3H_6Br)$ (1 equiv.) in the presence of excess NaH. First, the hydroxyl groups of $CB8(OH)_n$ were deprotonated with NaH and then underwent a S_N2 nucleophilic substitution reaction with propyl bromide groups of $TPP-4(OC_3H_6Br)$ to form polyethers.

The developed **PCN** having 3D network structure was fully characterized using a number of different techniques to reveal its structure and composition (¹H NMR, FT-IR, XPS, EDX), morphology (TEM, SEM, XRD) and thermal behavior (TGA) (Figs. S13–S18). Although **PCN** is insoluble



Scheme 1. Synthesis of PCN and its precursors: (i) K₂S₂O₈, K₂SO₄, H₂O, 85 °C, 12 h, N₂ (g), (ii) BBr₃, DCM, 0 °C, 48 h, (iii) DMF, K₂CO₃, 1,3-dibromopropane, RT, 72 h, (iv) DMSO, NaH, RT, 72 h.

in any common solvent (aqueous and organic), we dispersed it in DMSO- d_6 by overnight stirring at room temperature and then its ¹H NMR spectrum was recorded. As shown in Fig. S13, ¹H NMR spectrum shows clearly the characteristics signals for the protons of CB [8], porphyrin and phenyl units. TEM image of PCN displayed porous structure with the average particle size about 20-30 nm (Figs. 1a and S14a). The SEM images further confirmed the porous morphology of this sample (Figs. 1b and S14b). The SEM/EDX elemental mapping of PCN was presented in Fig. 1c. Fig. S15 compares the EDX spectrum of PCN with its monomer, TPP-4(OC₃H₆Br). The decrease in the percentage of Br from 6.26% in porphyrin monomer to 0.32% in the final COF, clearly confirmed the successful synthesis of PCN. The small amount of Br (0.32%) in the EDX spectrum of PCN can be attributed to the end groups of the framework. The chemical and elemental composition of PCN was further studied by XPS (Fig. 1d). The C1s XPS spectrum can be resolved into seven components 284.10, 284.75, 285.25, 286.04, 286.88, 287.67, and 288.90 eV that correspond to C=C, C-C, C-N, C-O, C=N, C=O, and N-C=O bonds, respectively. Two distinct peaks at 531.5 and 533.05 eV in the O1s spectrum represent the C=O and C-O components. The N1s spectrum can be deconvoluted into four peaks with the binding energies of 398.35, 399.41, 400.10, and 400.70 eV corresponding to C-N=C of porphyrin core, C–NH–C of porphyrin core, N(C)₃ of **CB** [8] and -N-(C=O)- of **CB** [8], respectively. The Powder XRD pattern of **PCN** showed a crystalline structure with well-defined diffraction peaks at 2θ = 7.2°, 18.1° and 20.4° (Fig. S16). TGA of **PCN** was conducted to measure the weight loss and thermal stability of the sample in the temperature range of 25–950 °C with a heat rate of 10 °C min⁻¹ under N₂. TGA curve (Fig. S17) exhibited three types of decomposition. An initial mass loss (below 200 °C, 10%) is attributed to the elimination of physically adsorbed water molecules. The subsequent mass losses (26%) started at 200 °C is correlated with the organic degradation (loss of free ether groups, benzene rings and CB8) and from 700 °C sample itself begun to decompose. Even at 700 °C, only 36% of weight loss was observed indicating the high thermal stability of **PCN**. The total weight loss of the sample (25–950 °C) was around 93%. FT-IR spectrum of **PCN** was illustrated in Fig. S18.

3.2. Preparation and characterization of GO, ERGO and ERGO/Ni@PCN

GO was synthesized using the improved Hummers' method (Tour's method) [63]. We examined both chemical and electrochemical methods for the reduction of **GO** and found the electrochemical



Fig. 1. (a) TEM image, (b) SEM image, (c) the corresponding SEM/EDX elemental mapping images (SEM image scale bar is 4 µm) and (d) XPS data of PCN.

reduction procedure to be the most effective in producing reduced **GO** with lower oxygen to carbon ratio than the chemically reduced one. When we explored the chemical reduction using ascorbic acid, for instance, the resulting **RGO** yield was relatively low. Furthermore, the chemical reduction of **GO** required longer processing time. Therefore, we implemented the electrochemical reduction method as it is a simple, fast and highly efficient technique. The catalyst modified-FTO was fabricated with layer-by-layer (LBL) assembly technique using negatively charged **GO** and positively charged **Ni@PCN** followed by an electrochemical reduction procedure [55]. Since **GO** has a higher negative charge density than **ERGO**, it is much more convenient to reduce **GO** after layer-by-layer assembly of electrode to enable the formation of stronger electrostatic interactions. Fig. 2 represents the fabrication procedure of **ERGO/Ni@PCN** electrode.

The electrochemical reduction of **GO/Ni@PCN** was confirmed by cyclic voltammetry scans in 0.1 M PBS where they exhibited a welldefined cathodic peak in the first cycle (Fig. S19 a). This large change in cathodic current is attributed to the electrochemical reduction of oxygen-containing functional groups of graphene oxide [64]. In the first run, the electrochemical reduction of **GO₁/Ni₂@PCN** occurs at a more positive potential (-0.65 V) than that of pure **GO** (Fig. S19b) which is around -0.80 V. This cathodic peak was not observed in the successive scans indicating that the reduction process is irreversible.

The morphology of **GO** was studied by TEM and SEM. From the TEM image shown in Fig. 3a, single-layered **GO** was formed with flake-like structure, smooth surface, and some wrinkles. SEM image of **GO** (Fig. 3b) displayed wrinkled sheets that were randomly connected forming a crumpled solid. The surface morphology of **ERGO** and **ERGO**₁/**Ni**₂@**PCN** modified FTOs were also studied using SEM. As shown in the SEM image of **ERGO** (Fig. 3c), electrochemical reduction of **GO** resulted in less intense wrinkled sheets that are further apart and have a rougher surface compared to **GO**. The SEM image of **ERGO**₁/**Ni**₂@**PCN** presented many porous micro structures owing to **PCN** along with stacked **ERGO** sheets at a low magnification (Fig. 3d).

The crystalline structures of the samples were characterized by XRD. Fig. 4a compares the XRD patterns of powder graphite flakes, **GO**, **ERGO** and **ERGO**₁/**Ni**₂@**PCN** samples coated on FTO. The diffraction peaks of graphite flakes and exfoliated **GO** appeared at 26.6° and 12.1° with dspacing of 0.33 and 0.73 nm, respectively. The diffraction peak of **GO** at 12.1° completely disappeared after reduction, signifying the absence of



Fig. 3. (a) TEM image of GO powder, SEM images of (b) GO powder, (c) ERGO and (d) ERGO₁/Ni₂@PCN thin films (top view on FTO glass).

unreduced graphene oxide as reported in the literature [65,66]. The three latter sharp peaks ($2\theta = 26.5$, 33.6 and 37.7°) correspond to signals from FTO glass. The XRD spectrum of **ERGO₁/Ni₂@PCN** demonstrated an extra peak at 8.7° which is equivalent to an interlayer spacing of 1.02 nm. The same peak was also observed in the XRD pattern of **Ni₂@PCN** (Fig. S20). This increase in interlayer spacing confirms the formation of **Ni₂@PCN** composite on reduced graphene oxide. The structural changes upon the synthesis of **ERGO₁/Ni₂@PCN** was further analyzed by Raman spectroscopy (Fig. 4b). All three samples (**GO**, **ERGO** and **ERGO₁/Ni₂@PCN**) presented characteristic G and D bands in the region between 1000 and 2000 cm⁻¹. The G and D bands were located around 1592 cm⁻¹ and 1344 cm⁻¹, respectively, in **GO**. The intensities of both bands were almost equal in **GO**, where I_D/I_G was about 0.98. However, in **ERGO** and **ERGO₁/Ni₂@PCN** the G band was shifted slightly to 1581 cm⁻¹ and the D-band intensity increased



Fig. 2. Schematic representation of preparation procedure of ERGO1/Ni2@PCN modified FTO electrode.



Fig. 4. (a) XRD patterns and (b) Raman spectra of graphite flakes, GO, ERGO and ERGO₁/Ni₂@PCN.

resulting in a larger $I_D/I_G\sim 1.1$ which was in similar to the value reported by Renteria et al. [67]. This is due to the increase in defect concentration present in **ERGO** (vacancies, disorders) compared to **GO** and increase in sp² restoration [68].

The FT-IR spectra of the studied sample were displayed in Fig. S21. The main characteristic transmission signals in GO, ERGO, and ERGO₁/Ni₂@PCN samples include a broad peak at approximately 3470 cm⁻¹ attributed to O–H stretching in carboxyl groups, a weak peak at about 1740 cm⁻¹ corresponding to C=O stretching in carbonyl and carboxyl groups that was reduced upon reduction. Moreover, an intense peak at around 1620 cm⁻¹ was assigned to C=C skeletal vibration of unoxidized graphitic domain [69]. Small transmission peaks appeared at around 2800-2950 cm⁻¹ can be assigned to stretching vibrations of C–H and –CH₂ groups [70].

In order to better understand the changes in chemical composition caused by electrochemical reduction and the bonding involved in the composite, XPS measurements were carried out. Fig. S22 displayed the XPS survey spectra of **GO** and **ERGO**. The obtained atomic percentage of elements revealed that the oxygen content was reduced by 50% after reduction of **GO** to **ERGO**, where C/O was found to be about 4.03 for **ERGO** and 1.90 for **GO**. The largest peak ~700 eV at both XPS survey spectra corresponds to fluorine from FTO. The XPS spectra of C1s and O1s for **GO** and **ERGO** (Fig. 5a and b) exhibited a noticeable decrease in oxygen content after reduction of **GO** to **ERGO**, which was shown by the decrease in intensities of C=O, COOH and C-O peaks as well as an increase in C-C/C=C peaks due to the partial respiration of the sp² network in graphene. As shown in Fig. 5a, the C1s spectrum of **GO** illustrated the characteristic peaks of C=C (284.6 eV) and C-C (285.6) as well as C-O (287.5 eV), C=O (288.1 eV) and a minute peak of COOH (289.3 eV) which correspond to its hydroxyl, epoxide, and carboxyl functional groups, respectively. The O1s spectrum of **GO** (Fig. 5a) showed two distinct peaks at 532.1 eV and 533.4 eV correspond to C=O/COOH and COH groups, respectively, with an extra peak at 534 eV due to the adsorbed water.

3.3. Evaluation of the electrocatalytic HER activity of ERGO/Ni@PCN

Electrochemical studies were begun with PCN containing Ni as



Fig. 5. High-resolution XPS spectra and of C1s and O1s for (a) GO and (b) ERGO.

cocatalyst. The effect of porphyrins and Ni centers on HER has been well studied in the last few decades [71,72]. Herein, the key features of the developed PCN to use as HER catalyst include the presence of electrochemically active non-metallated porphyrin core with rich multielectron redox chemistry and alkyl ether functionalities that can donate electrons, CB [8] macrocycle as an efficient macrocyclic host with its carbonyl portals that can coordinate with water and metal cocatalyst (Ni) for efficient energy transfer as well as its large hydrophobic cavity which is available to accommodate the guest molecules and store produced gases [73,74]. In this context, electrocatalytic HER performance of Ni2@PCN containing 47% Ni (weight ratio of nickel acetate to PCN is 2:1) was investigated in different electrolytes including acidic (0.05 M H₂SO₄), neutral (0.1 M PBS) and basic (0.1 M KOH) by conducting LSV measurements with scan rate of 10 mV s^{-1} in the Ar-saturated systems. As shown in Fig. S23, Ni₂@PCN displayed negligible performance in acidic and neutral mediums with very low cathodic current densities and large onset potential values, however its HER activity was considerable in 0.1 M KOH, with the lowest onset and $\eta@10 \text{ mA cm}^{-2}$ potentials of -253 mV and -894 mV, respectively. Consequently, all electrochemical studies were performed in 0.1 M KOH electrolyte.

In order to enhance the electrocatalytic performance of Ni@PCN in alkaline medium, a layer of **GO** was integrated into the catalytic system. When the positively charged Ni₂@PCN is added to the GO layer on FTO, the electrostatic interaction between the oppositely charge systems can provide a strong driving force for the assembly between the two entities. Additional interactions, such as π - π * stacking and van der Waals force between GO and Ni@PCN layers can also expand the stability of the resulting electrode [75]. Herein, five GO/Ni@PCN electrodes were prepared by varying Ni and GO contents. These samples were fabricated by first drop-casting a layer of GO ink over a clean FTO followed by a layer of Ni@PCN. The LSV curves of the GO containing electrodes were presented in Fig. 6a and compared to the bare FTO. The kinetic parameters were estimated using Tafel plots which were retrieved from the linear regions of the LSV curves by plotting overpotential against log current density. The obtained electrochemical parameters of all samples were listed Table S1. Although the incorporation of GO improved the performance of the composites; the effect of varying GO content was not as substantial as nickel. Increasing the weight ratio of GO from 0.5 to 1 in the samples with double amount of nickel acetate (with respect to PCN) increased the HER performance, while further increase in GO content significantly decreased the HER activity. This can be explained by the fact that extra GO in the catalyst may saturate the active site density. Among these electrodes, the preeminent HER activity was observed by $GO_1/Ni_2@PCN$ owing to its lowest onset and $\eta@10$ mA cm^{-2} potentials of -145 mV and -879 mV, respectively, as well as its largest exchange current density of 0.360 mA cm^{-2} . The electrocatalytic HER performance of GOn/Ni2@PCN electrode improved in the order of GO₂/Ni₂@PCN < GO_{0.5}/Ni₂@PCN < GO₁/Ni₂@PCN. The nickel content of the optimum GO1/Ni2@PCN electrode was calculated to be 47% (with respect to PCN) and in the entire catalytic system it was less than

20%.

The activity of GO/Ni@PCN catalysts was further upgraded by providing a conductive support system using reduced graphene oxide. All five GO/Ni@PCN electrodes with different Ni and GO contents were electrochemically reduced using consecutive cyclic voltammetry scans in 0.1 M PBS (see Experimental section for more details) and then their electrocatalytic HER behavior was tested. Fig. 6 shows the LSV polarization measurements of ERGO containing electrodes. The corresponding electrochemical and kinetic parameters of all reduced electrodes were summarized in Table S2. Based on the results, all ERGO/Ni@PCN electrodes displayed better HER activities than before reduction, having lower onset and $\eta@10 \text{ mAcm}^{-2}$ potentials. Among these, ERGO₁/ Ni2@PCN presented outstanding electrocatalytic activity with onset potential of -30 mV, $\eta@10 \text{ mA cm}^{-2}$ of -717 mV, Tafel slop of -522mV dec $^{-1}$, exchange current density of 0.771 mA cm $^{-2}$ and TOF value of 0.048 s^{-1} which indicated better electrocatalytic activity in comparison to similar studies [50,51]. Fig. 6c compares the Tafel plots of optimum ERGO₁/Ni₂@PCN catalyst with GO₁/Ni₂@PCN and Ni₂@PCN.

To better comprehend the effect of impregnation and the mechanism of electron transfer, electrochemical analysis of the binary nanohybrids (Ni2@PCN and ERGO/PCN) were studied under optimum conditions. Fig. S24 compares the LSV curves of ERGO1/Ni2@PCN, Ni2@PCN, and ERGO/PCN samples measured with scan rate of 10 mV s⁻¹ in 0.1 M KOH. ERGO₁/PCN-modified FTO degraded slowly into the electrolyte then eventually completely peeled off. It was remarked that implanting nickel ions reduces the onset potential and upsurges the stability for the optimum sample. Since nickel ions behave as interfacial linkers, they trigger electron transfer and prevent the repulsion between PCN and ERGO layers. Furthermore, Ni2@PCN-modified FTO behaved similarly but with even lower current density values. This suggests that presence of ERGO significantly enriches the catalytic activity (around 40%) which could be observed by the comparing $\eta@10mAcm^{-2}$ of Ni₂@PCN and ERGO1/Ni2@PCN as shown in Fig. S24. We also studied effect of PCN-modified FTO alone. This resulted in an unstable coating with small current density values and $\eta@10$ mAcm⁻². These results imply that the outstanding HER activity of the ERGO1/Ni2@PCN arise from the synergistic collaborations of all three entities together.

The effect of varying the number of layers on FTO was also investigated for optimum **ERGO**₁/**Ni**₂@**PCN** catalyst in 0.1 M KOH (Fig. S25). This was done by alternating deposition of a layer of **GO** then a layer of **PCN**, respectively. From the results, increasing the number of layers had no significant change in the HER performance of catalyst, while the catalyst with one layer **GO** and one layer **PCN** poses lowest onset potential; therefore, no further investigations have been made on layering.

To gain further intuition into the HER electrocatalytic activity of ERGO₁/Ni₂@PCN, EIS measurements were performed from 0.1 Hz to 100 kHz at -0.6 V (vs. RHE) in 0.1 M KOH. Fig. 7a compares Nyquist plots of optimum ERGO₁/Ni₂@PCN electrode with GO₁/Ni₂@PCN and ERGO. The Nyquist plot of ERGO₁/Ni₂@PCN showed two semicircles; with the first being negligible in comparison to the one at low frequency.



Fig. 6. LSV curves for (a) GO/Ni@PCN catalysts and (b) ERGO/Ni@PCN catalysts with varying Ni and GO content measured with scan rate of 10 mV s⁻¹ in 0.1 M KOH, (c) Tafel plot of optimum ERGO₁/Ni₂@PCN catalysts compared to GO₁/Ni₂@PCN and Ni₂@PCN.



Fig. 7. (a) Nyquist plots of ERGO₁/Ni₂@PCN, GO₁/Ni₂@PCN and ERGO catalysts measured at -0.6 V vs RHE in 0.1 M KOH. (b) The capacitive currents at 0.8 V as a function of scan rate ($\Delta j = j_{anodic}$ - $j_{cathodic}$).

The diameter of the first semicircle, which is associated with hydrogen adsorption was around of 60 Ω (R₁), while the diameter of second semicircle, which is related to the resistance to the HER kinetics [65], was found to be around 1000 Ω (R₂). The total charge-transfer resistance (R_{ct}) of **ERGO₁/Ni₂@PCN** was about 1060 Ω . The Nyquist plot of the **ERGO** and **GO₁/Ni₂@PCN** samples showed two semicircles and one semicircle, respectively, with R_{ct} values of 2800 and 2200 Ω . The Lowest R_{ct} of **ERGO₁/Ni₂@PCN** resulting in the fast electron transfer at the electrode-electrolyte interface, which can be due to the increased π -conjugated electronic structure of the sample. Furthermore, the absence of a Warburg impedance implies a fast-ionic transportation and a kinetically controlled electrochemical reaction.

The electrochemical double layer capacitance (C_{dl}) of optimum $ERGO_1/Ni_2 @PCN$ catalyst was measured in comparison with ERGO

and **GO**₁/**Ni**₂@**PCN** to estimate the electrochemical active surface area of the catalysts. Cyclic voltammetry measurement was performed in the non-faradaic region (-0.1 to -0.2 V vs Ag/AgCl) at scan rates from 50 to 100 mV s⁻¹. Experimental details were given in ESI. According to the results (Figs. 7b and S26), **ERGO**₁/**Ni**₂@**PCN** showed the highest C_{dl} of 185.1 µF cm⁻² compared to **GO**₁/**Ni**₂@**PCN** and **ERGO** with C_{dl} values of 96.5 and 63.9 µF cm⁻² values, respectively. This implies that reduction of **GO** results in an increased electroactive surface area.

Based on these results, the decrease in R_{ct} values from 2200 Ω to 1060 Ω and increase in C_{dl} values from 63.9 μ F cm⁻² to 185.1 μ F cm⁻² upon impregnation of nickel ions and **PCN** into **ERGO** indicate the significance of incorporating an electron rich entity of porphyrin, bulky stabilizing units of **CB** [8] and strong interfacial metal linkers.

The electrochemical behavior of the optimum ERGO1/Ni2@PCN



Fig. 8. (a) LSV polarization curves of **ERGO**/Ni₂@**PCN** obtained at 10 mV s⁻¹ in concentrated acidic and basic electrolytes compared to 0.1 M KOH, (b) The capacitive currents at 0.8 V as a function of scan rate for **ERGO**/Ni₂@**PCN** in 1 M KOH, (c) the Nyquist plot of **ERGO**/Ni₂@**PCN** recorded at -0.4 V vs RHE in 1 M KOH, (d) chronoamperometry of **ERGO**/Ni₂@**PCN** at -1.2 V vs Ag/AgCl in 1 M KOH and the corresponding polarization curves before and after 12,000 s stability experiment.

sample was further explored in concentrated electrolytes: 0.5 M H₂SO₄ and 1 M KOH. As can be seen in Fig. 8a, The ERGO1/Ni2@PCN catalyst was found to be rather inactive in 0.5 M H₂SO₄ as it showed a very low cathodic current density with high onset potential. The efficiency of ERGO1/Ni2@PCN was found to be much more prominent in highly concentrated basic medium, with improved onset potential of -20 mV, $n@10 \text{ mA cm}^{-2} \text{ of } -360 \text{ mV}$ and TOF value of 0.351 s⁻¹. The poor activity of electrocatalyst in acidic medium could be attributed to the protonation of pyrrolic nitrogen of porphyrins. This positively charged group in turn prompts repulsive interactions with positively charged nickel ions and prevents charge transfer to ERGO. Moreover, PCN is usually more soluble in acidic medium, which permits the protonation of carbonyl groups in **CB** coordinate hence, preventing its interaction with ERGO. The better performance in alkaline medium on the other hand, could be conveyed by the additional electrostatic interactions between the deprotonated negatively carboxylic acid groups on ERGO and the nickel ions which result in more stable hybrid films with faster electron transfer. The Cdl value of this electrode in 1 M KOH was measured (Fig. 8a) to be even more noteworthy $(1.67 \text{ mF cm}^{-2})$ than diluted 0.1 M KOH, suggesting better electrocatalytic activity and large available electroactive surface area. EIS measurements in 1 M KOH (Fig. 8c) showed two semicircles in Nyquist plot with very low R_{ct} value of 210 Ω which is much lower than its R_{ct} in 0.1 M KOH (1060 Ω). This signifies greater resistance for electron transfer in dilute KOH electrolyte, possibly due to the presence of excessive bulky water molecules that hinder transport. These results are in line with exchange current density values for both mediums where in 1 M KOH, ERGO1/Ni2@PCN exhibited larger value of exchange current density $(1.14 \text{ mA cm}^{-2})$ which infers faster kinetics. The obtained R_{ct} value of 210 Ω was found to be lower than in analogous studies reported in the literature such as [ERGO@CoTMPyP]7 and CoTMPyP/ERGO with Rct of 283 and 312 Ω, respectively, in alkaline media [54,55]. The impedance responses of ERGO1/Ni2@PCN in both 0.1 M and 1 m KOH can be demonstrated by a simple Rendles equivalent circuit with a combination of two capacitance (Q₁, Q₂) and resistance (R₁, R₂) placed in parallel (see insert of Fig. 8c). These circuit elements are linked to the high (Q1, R1) and the low frequency (Q_2, R_2) capacitive loops, respectively [50]. The resistance R_s represents uncompensated solution resistance, which was around 15 Ω in 1 M and 50 Ω in 0.1 M KOH for **ERGO**₁/Ni₂@PCN. Table 1 compares the HER electrocatalytic activity of ERGO1/Ni2@PCN in 0.1 M and 1 M KOH aqueous solutions.

Stability of the electrode is an important factor for practical applications of electrocatalysts. The stability of ERGO₁/Ni₂@PCN for H₂ evolution was evaluated (Fig. 8d) via chronoamperometric (CA) method under static potential of -1.2 V vs Ag/AgCl (-0.236 V vs. RHE) in 1 M KOH. ERGO₁/Ni₂@PCN electrode exhibited sufficient stability and the current density remained almost constant for at least 12000s. Moreover, the LSV polarization curve of the ERGO₁/Ni₂@PCN catalyst measured after the stability experiment was almost unchanged signifying its superior stability in 1 M KOH (see insert of Fig. 8d). CA experiment of ERGO₁/Ni₂@PCN was also performed in 0.1 M KOH and demonstrated its stable catalytic activity for 6000 s under a constant potential of -1.2 V vs Ag/AgCl (Figs. S27a and b).

The amount hydrogen produced was calculated from the Faraday's

Table 1

Electrochemical paramete	ers for ERGO ₁	/Ni2@PCN in	0.1 N	/I and 1 M	KOH.
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Obtained parameters	0.1 M KOH	1 M KOH
Onset/mV vs RHE	-30	-20
η@10 mA cm ⁻² /mV	-717	-360
Tafel slope/mVdec ⁻¹	552	413
Exchange current density/mA cm ⁻²	0.771	1.140
Faradaic efficiency/%	86.7	93.6
Amount of H ₂ produced/mmol h ⁻¹ g ⁻¹	15.6	27.5
$C_{dl}/mF cm^{-2}$	0.185	1.67
R_{ct}/Ω	1060	210

law (see electrochemical calculations, ESI). Accordingly, **ERGO**₁/ **Ni**₂@**PCN** was able to produce 15.6 mmol $h^{-1}g^{-1}$ of hydrogen theoretically in 0.1 M KOH and 27.5 mmol $h^{-1}g^{-1}$ of hydrogen in 1 M KOH, with faradaic efficiencies of 86.7% and 93.6%, respectively. The amount of evolved hydrogen was calculated to be 9.3 mmol $h^{-1} g^{-1}$ for **GO**₁/ **Ni**₂@**PCN** and 6.6 mmol $h^{-1} g^{-1}$ for **Ni**₂@**PCN**. Fig. S30 compares the amounts of hydrogen produced by the catalysts studied in this work.

The excellent catalytic performance for ERGO1/Ni2@PCN could be rationalized as follows: (1) ERGO demonstrates unique electronic features owing to its zigzag edges, unsaturated carbon atoms and numerous defects which can provide catalytic active centers for hydrogen evolution [76]. Owing to its good conductivity, ERGO accelerates electron transport and provides a negatively charged support. Observing lower Tafel slope and charge transfer resistance in presence of ERGO highlights its role in driving the kinetics of the reaction toward favoring HER subsequently decreasing the charge transfer at the and catalyst-electrolyte interface; (2) the high π -conjugation system of the central N₄ atoms of porphyrin core in **PCN** permits π -electron delocalization bring about efficient charge transfer to ERGO laver. Additionally, the intermolecular hydrogen bonding and the high electronegativity of the central N₄ in the assembled porphyrin improves the charge transfer from the porphyrin to graphene [57]; (3) nickel ions behave as interfacial linkers that speed up electron transfer, permit electrostatic interactions of PCN with ERGO layer and boost the adsorption of hydrogen onto catalyst surface as well as adsorb to hydroxide ions that form during water splitting [77]; (4) CB [8]s provide the chemical stability of PCN moiety and prevent ERGO from stacking [37,78]. Owing to carbonyl groups on the periphery of cavity, CBs show high electron density that leads to cation receptor behavior of these structures, hence, the carbonyl portals of CB [8] can be coordinated with Ni^{2+} ions and stabilized them in the **PCN** structure. Moreover, π -conjugated structure of porphyrin can drag them to make agglomerations which can be prevented by having CB in the structure [22]. On the other hand, the large cavities of CB [8]s are available to encapsulate the produced hydroxide ions to inhibit undesired reactions [79] as well as to hold the produced H₂ gases to further use for hydrogen storage targets [80]. In one of our previous studies where we successfully used our developed TPP-CB7-TiO2@Pt composite for electrophotocatalytic hydrogen generation from water splitting, the experiments clearly revealed that the presence of CB improves the photocatalytic HER activity and stability of the catalyst [37]. To conclude, the presence of **CB**s in the developed PCN provide the chemical stability of the assembly, stabilize the metal ions and consequently improve the HER efficiency of the assembly.

All in all, the coordinate interaction between Ni²⁺ and the conjugate rings of the **PCN** molecules, as well as the π - π stacking and van der Waals forces between the **PCN** molecules and **ERGO** can greatly facilitate the flow of electrons. On the basis of the aforementioned results, a possible mechanism for the water reduction on the noble-metal-free conjugated system can be concluded. The applied potential induces electron transfer from electron rich **PCN** to **ERGO** by means of nickel ions. The electrons are then captured by water molecules in electrolyte at **ERGO** interface and subsequently, are reduced into hydrogen.

The morphology and chemical composition of ERGO₁/Ni₂@PCN electrode were examined using SEM and XPS analyses, before and after 12000s CA experiment in 1 M KOH. From Figs. S28a and b, the morphology of ERGO₁/Ni₂@PCN electrode remained almost unchanged after the stability test. SEM/EDX elemental mapping images showed similar morphology before and after catalysis where Ni was uniformly distributed in the catalyst. As it is shown in Fig. S29 a and b, comparable XPS spectra were obtained for C 1s, O 1s and Ni 2p before and after 12000s catalysis under hydrogen production conditions implying that the electrocatalyst did not experience any significant change in its chemical composition.

The XPS elemental survey indicated that 71.3% of the composite was carbon, 1.41% was nitrogen, 23.2% was oxygen and the remaining was

nickel. From the XPS survey spectra, the C/O value of the catalyst after CA experiment was found to be 3.10 which was comparable to before CA (3.47). The Ni2p spectrum was divided into six peaks with their corresponding satellite peaks. The peaks around 855.7 eV (Ni2p_{3/2}) and 873.1 eV (Ni2p_{1/2}) with their satellites at 861.0 and 878.4 eV, respectively, can be attributed to the NiO species. The other peaks at 857.0 eV (Ni2p_{3/2}, with satellite peak at 862.2 eV) and 874.4 eV (Ni2p_{1/2}, with satellite peak at 879.8 eV) are assigned to Ni(OH)₂ species. Furthermore, minor amount of Ni⁰ was observed by having the peaks at 852.8 and 870.1 eV, which indicate possible reduction of nickel ions to metallic nickel. The C1s spectra displayed two extra peaks at 292.5 and 295 eV after CA experiment which are linked to K2p_{3/2} and K2p_{1/2} signals from residual potassium in PBS solution [67]. Similarly, O 1s showed an extra peak 536 eV due to the K₁L₁L₂₃ Auger peak of sodium ions present in PBS [81].

4. Conclusions

A new highly efficient HER electrocatalyst was developed through the LBL coating of GO nanosheets and Ni@PCN composite, respectively, over FTO in combination with an electrochemical reduction procedure. PCN was successfully synthesized via the covalent conjugation of CB8 (OH)_n to TPP-4(OC₃H₆Br) and then it was fully characterized. Owing to the presence of CB [8] and electroactive porphyrin cores in the multifunctional supramolecular structure that was loaded with Ni and supported on the high conductive and negatively charged graphene nanosheet, ERGO/Ni@PCN was found to be a promising candidate for HER electrocatalysis in alkaline medium. Effect of varying the contents of Ni and GO on the HER activity of ERGO/Ni@PCN was explored in 0.1 M KOH and the excellent electrocatalytic performance was observed for ERGO1/Ni2@PCN with the double amount of nickel acetate and equal amount of GO with respect to PCN. Further studies demonstrated that the HER activity of ERGO1/Ni2@PCN was significantly enhanced in 1 M KOH, where it showed the lowest onset and $\eta@10$ mA cm⁻² potentials of -20 mV and -360 mV, respectively, large exchange current density of 1.14 mA cm⁻² and C_{dl} of 1670 mF cm⁻² as well as low charge transfer resistance of 210 Ω specified a fast reaction. The optimum ERGO₁/Ni₂@PCN as a proficient HER electrocatalyst produced 27.5 mmol $g^{-1} h^{-1}$ and 15.6 mmol $g^{-1} h^{-1}$ of hydrogen in 1 M KOH and 0.1 M KOH, respectively, which are comparable and even better than previously reported porphyrin/graphene-based HER electrocatalysts (Table S3) [6,8,34,37,82–85]. It is envisaged that this work may introduce a facile path to design a wide range of low-cost and high-performance organic entities for HER.

CRediT authorship contribution statement

Bouthaina Aoudi: Investigation, Implementation research, Data curation, Formal analysis, Writing-original draft, Writing – review & editing. Aisan Khaligh: Implementation research, Data curation, Formal analysis, Writing- original draft, Writing – review & editing. Yasaman Sheidaei: Data curation. Dönüs Tuncel: Supervision, Conceptualization, Funding acquisition, Writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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