Galvanic exchange at layered doubled hydroxide/N-doped graphene as an in-situ method to fabricate powerful electrocatalysts for hydrogen evolution reaction

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Abstract

Introducing a novel strategy for growing dispersed metal nanoparticles at reduced graphene oxide (rGO) and nitrogen-doped GO (rNGO), this work aimed to design Pt-free electrocatalysts for water splitting. For this purpose, gold nanoparticles were fabricated by the *in-situ* galvanic exchange of layered double hydroxide (LDH) metals on rGO and rNGO. The significant roles of the galvanic exchange method, LaNi-LDH, and the Au nanoparticles synthesized on the rGO/rNGO-LaNi-LDH surface (Au[@]rGO/rNGO-LaNi-LDH) were investigated via a variety of methods and certain novel properties such as nitrogen-metal bridge bonds between the metal component of Au[@]LDH and the nitrogen component of rNGO were established, which indicated the semi-nanorod morphology of the Au[@]rGO/rNGO-LaNi-LDH thus produced. Electrochemical studies were used to reveal an onset potential of only –80 mV *vs.* RHE at an exchange current density of about 10 mA cm⁻² with a small Tafel slope of 60 mV dec⁻¹ for the hydrogen generation reaction in a 0.5 mol L⁻¹ H₂SO₄ solution. The isolated island architecture of rNGO/LaNi-LDH and rNGO/Au[@]LaNi-LDH were found to promise rich and active sites to be exposed, which allow for the effective interaction of the reactants (*e.g.*, protons) with these active sites.

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1. Introduction

Concerns about the worldwide energy crisis and the associated environmental issues due to the burning of fossil fuels have stimulated the quest for sources of clean and renewable energy [1,2]. The search for green energy in recent years has drawn increasing attention to hydrogen as a promising source of energy in future [3,4]. Molecular hydrogen offers a good potential for green energy as it is an environmentally-friendly gas with a high energy content per unit mass. Furthermore, water does not produce greenhouse gasses or any other harmful chemicals when consumed to generate H₂ [5,6]. Water splitting is the technique used to generate H₂ by electrochemical and photochemical methods, in which an electrocatalyst (i.e., an electrochemical or a photochemical catalyst) plays the key role in the successful water splitting process. Study has revealed that a suitable electrocatalyst must have the following five properties [7,8]: 1) an atomic-scale size to increase the number of active sites, 2) a high aspect ratio to improve the catalytic performance per geometric area, 3) a porous structure to enhance the rapid mass transport of reagents, 4) an excellent electrical conductivity to facilitate electronic transfer, and 5) good physicochemical properties to yield a high-performance electrocatalyst activity [9,10]. The most efficient catalysts used for hydrogen generation are metals of the platinum group. However, noble metals such as platinum are not in abundance in the earth's crust, compared to other elements, to provide adequate supplies of the catalyst required for hydrogen evolution reaction at a scale comparable to the world energy demand [11]. Thus, research conducted to address electrocatalysts for hydrogen generation has been directed toward the application of molybdenum and tungsten sulfides for the hydrogen evolution reaction [12–14]. Both computational and experimental results have confirmed their

hydrogen generation activity [15,16]. Transition metal sulfides are typical layered materials which have proved to be highly active and versatile electrocatalysts for the hydrogen evolution reaction in acidic solutions [17–20]. Another type of clear layered materials is the layered double hydroxides (LDH) with many such applications as electrocatalysts, photocatalysts, and intercalated catalysts [21–24]. One application of LDH, which we will use below to compare with transition metal sulfides, is its electrocatalytic application. It has, in fact, been widely used with a large number of metals such as Ni and Co in electrocatalytic reactions [21].

The galvanic exchange, or replacement, reaction is a fundamental oxidation-reduction reaction which has drawn much attention as a pioneering method to design the legendary nano-structures. It is a spontaneous electrochemical reaction that can be monitored within a temporal target. Furthermore, it can produce varying compositions with different metallic nanostructures through combining different ratios of metals. The last but not least advantage is the unique morphology of the last exchanged nanostructure [25,26]. Xia and co-workers obtained hollow nanotubes of the Au-Ag alloy by titration of Ag nanowires using HAuCl_4 solution [25,26]. Moreover, efforts have been directed at producing nanoporous surfaces in Cu-Ni [27], synthesizing platinum nanofiber/nanotube junction structures by direct mixing of silver nanowire in a platinum solution [28], or forming hollow gold and platinum shell nanoparticles via the transmetallation reaction [29]. However, there still exist much more unknown materials in need of investigation despite many experimental works conducted to use the galvanic exchange reaction for the manufacturing of novel structures of interest.

In the present study, a novel synthetic strategy (i.e., the galvanic exchange reaction) was used to grow dispersed gold nanoparticles with the assistance of Lanthanum-Nickel Layered Double Hydroxide (LaNi-LDH) on the different media of graphitic plates of

reduced graphene oxide (rGO) or nitrogen-doped reduced graphene oxide (rNGO). The synthesis of gold in the lanthanum-nickel layered double hydroxide/reduced graphene oxide (rNGO/Au[@]LaNi-LDH) and lanthanum-nickel layered double hydroxide/nitrogen-doped reduced graphene oxide (rGO/Au[@]LaNi-LDH) surfaces was achieved *via* a two-step method; i) loading different LDH percentages (by ultrasonic irradiation) on the surfaces of rNGO and rGO, and ii) using the simple galvanic exchange of LDH's metals (e.g., Ni) with gold in an acidic solution to form gold nanoparticles on the synthesized (rGO/Au[@]LaNi-LDH and rNGO/Au[@]LaNi-LDH) surfaces. The new nanomaterials (i.e., rGO/Au[@]LaNi-LDH and rNGO/Au[@]LaNi-LDH) provide several key advantages. Firstly, they are produced in a direct-step synthesis with no special instruments or harsh conditions required. Secondly, the Au nanoparticles are fabricated by *in-situ* formation on rGO/LaNi-LDH and rNGO/LaNi-LDH environments. This allows for the aggregation of Au nanoparticles to be prevented. Finally, the excellently active metal-nitrogen interaction (M-N) provides a pathway for electron transfer. To the best of the authors' knowledge, this is the first report on the galvanic exchange of LDH metals employing nitrogen-metal/LDH interaction, LDH, and graphitic plates to disperse gold nanoparticles in order to improve upon the performance of LDH and N-doped graphene oxide used for the electrochemical hydrogen evolution. These extraordinary synthetic electrocatalysts are comparable, or even superior, to the different transition metal sulfides in such respects as onset potentials, Tafel slope, and current density.

2. Experimental

2.1. Reagents

Graphite, HNO₃, H₂SO₄, Ni(NO₃)₂·6H₂O and La(NO₃)₃·6H₂O were purchased from

Merck. Nafion solution (5.0 wt.% in lower aliphatic alcohols and water) and ammonium hydroxide solution were purchased from Aldrich. All other chemicals used in this investigation were of analytical grade and were purchased from Merck. Deionized water was used for the preparation of all of the solutions.

2.2. Apparatus

Fourier-transform infrared (FT-IR) spectra of the nanocomposites were investigated using a JASCO 680 (Japan) spectrophotometer over the wavenumber of 400–4000 cm^{-1} . Transmission electron microscopy (TEM) was performed using a Philips CM120. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with the concentric hemispherical analyzer and VG Microtech twin anode XR3E2 X-ray source was used as incident radiation. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area of the nanocomposites. Using the Barrett–Joyner–Halenda (BJH) model, the pore volumes, and pore-size distributions were derived from the adsorption branches of the isotherms, while the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.989. Electrochemical measurements were performed in 0.5 mol L^{-1} H_2SO_4 solution at room temperature. The electrode potential was controlled by an Autolab electrochemical analyzer, Model PGSTAT 30 potentiostat/galvanostat (Eco–Chemie, The Netherlands). Data were acquired and processed (background correction) using the GPSE and FARA computrace software 4.9.007. A standard three-electrode cell, containing a platinum wire auxiliary electrode, a saturated Ag/AgCl reference electrode and the nanocomposites as working electrodes, was used.

2.3. Synthesis and preparation of graphene oxide and reduce graphene oxide

Modified Hummer's method was applied to synthesize graphene oxide (GO) from natural graphite powder [30]. Briefly, graphite powder (6.00 g, 325 meshes) was added into a solution containing 48 mL H_2SO_4 (98% w/w), 10.0 g of P_2O_5 and 10.0 g of $\text{K}_2\text{S}_2\text{O}_8$. The mixture was kept at 80 °C for 6 h. Then, the solution was diluted with 1.0 L of water, and it was left for 12 h. The mixture was filtrated and washed with 2.0 L of water. Afterward, 3.0 g of the pre-oxidized graphite was added to 240 mL conc. H_2SO_4 containing 30.0 g KMnO_4 under stirring and the temperature of the mixture was kept to be below 25 °C, using a water bath for 150 min. Then, the mixture was stirred at room temperature for 2 h, and it was diluted with 600 mL of water. Finally, 9.0 mL of 30% H_2O_2 was added to the above mixture. The mixture was filtered and washed with 1:10 HCl aqueous solution (2.0 L) to remove any metal ions. Then, it was repeatedly washed with water until the pH of the filtrate was neutral.

To prepare rGO, 30 mg GO was dispersed in water, and 150 mg NaBH_4 was added into the mixture in an ice bath for overnight. The mixture was filtered and washed with 100 mL water, and the solid sample was dried at room temperature.

2.4. Synthesis of nitrogen-doped reduced graphene oxide

Nitrogen-doped rGO was prepared using hydrothermal method. In a typical procedure, 70 mL of NH_4OH aqueous solution (30%) was added to 70 mg GO, which the reaction was kept at 40 °C with stirring for 1 h and sonicated for 30 min. Then, the reaction mixture was transferred into a 120 mL autoclave for hydrothermal reaction at 210–220 °C for 24 h. This hydrothermal step was also reduced NGO to rNGO. The resulted product was collected by centrifugation and washed with water and dried at room temperature.

2.5. Synthesis of nitrogen-doped rGO/LaNi-LDH and rGO/LaNi-LDH

Sonochemical method was used to synthesize rNGO/LaNi-LDH and rGO/LaNi-LDH. In the first step, rNGO and/or rGO suspension was prepared by dispersing of 140 mg rNGO and/or rGO in 25 mL of water. Then, 10 mL aqueous solution containing 81.0 mg $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 60.0 mg $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (with 2:1 molar ratio) was slowly added to the suspension of rNGO and/or rGO under N_2 atmosphere. The pH of the resulting mixture was maintained at 9–10 (by the addition of a 1.0 mol L^{-1} NaOH solution) and the mixture was stirred at 70°C for 2 h. The mixed solution was ultrasonicated for 2 h. Finally, the obtained suspension was filtrated, using Whatman filter paper, and washed thoroughly with water to remove any nitrate ions and dried at room temperature for overnight.

2.6. Preparation of the modified electrodes

Modified electrodes were prepared by dispersing of 5.0 mg of the electrocatalyst (nitrogen doped rGO/LaNi-LDH and/or rGO/LaNi-LDH) in 1.0 mL H_2O under ultrasonic agitation to form the electrocatalysts ink. Then, 10 μL of the ink was dropped on the surface of a glassy carbon electrode (GCE), and it dried at room temperature. After drying of the electrocatalyst, 10 μL Nafion solution (2.0 %) was dropped on the surface of the modified GCE, and it dried at room temperature after 10 minutes. For galvanic exchange reaction, the modified GCE was immersed into a 5.0 mL of 5.0 mmol L^{-1} AuCl_3 (in 0.1 mol L^{-1} H_2SO_4) solution for 20 min, to achieve Au^0 galvanic exchange reaction at the surface of the modified GCE.

3. Results and discussion

The intricate design of highly active and durable catalysts from earth-abundant elements has a great potential for replacing the different noble metal-based catalysts commonly employed in a range of useful (electro-) chemical processes. In this study, an inexpensive and powerful strategy is used to load noble metals at the surface of rGO or NrGO-intercalated La-Ni/LDH hybrids synthesized by the sonochemical method and the galvanic exchange reaction. The strategy leads to enhanced long-term cyclic stability, reduced onset potential, and increased current densities of the electrocatalysts for the hydrogen evolution reaction. The nitrogen doped graphene, which is covered by La-Ni/LDH and Au nanoparticles, produces morphologically nanorod-like sheets as a novel nanostructure hybrid created through the simple interaction between nitrogen and the metal component of Au[@]La-Ni/LDH. This interaction helps not only to induce more positive charges from LDH sheets onto the nitrogen-doped rGO but also to adsorb H⁺ for the hydrogen evolution reaction. Consequently, Au[@]LaNi-LDH/metals-nitrogen is a novel and clear interfacial covalent bond connection, which is a chemical and electronic coupling for achieving an excellent electrocatalyst in the hydrogen evolution reaction. A schematic representation of the loading process of rGO and/or rNGO on the Au[@]LaNi-LDH hybrid is shown in Figure 1. This includes a three-step process: the synthesis of nitrogen-doped rGO, the sonochemical intercalation of LDH, and the deformation of the hybrid by a galvanic exchange reaction. Once the electrocatalyst hybrid is deformed, a semi-nanorod of the graphitic plate is obtained by the simple galvanic exchange reaction. Upon deformation, a three-dimensional hybrid is formed, which participates more actively and efficiently in the hydrogen evolution reaction. **“Here Figure 1”**

3.1. Mechanism of rNGO/LaNi-LDH morphological deformation after galvanic exchange

reaction and LDH/metal-nitrogen semi-bonding

In the nitrogen-doped step, the high active NH_3 gas present in the ammonium solution attacks the GO sheets, resulting in some defects on the surface of GO. The defects may cause changes in the graphitic structure since the incorporation of pentagon–heptagon defects may induce strained domains in order to accommodate the graphitic edge dislocations. In the next step, pristine rNGO is treated with NaOH solution, which can gradually provide an alkaline medium to create brucite-like layers of LDH. Solvation of the metal salt and formation of the brucite-like layers of the LDH cause the positively charged LDH sheets to be adsorbed onto the anionic functional groups and the defective sites. This is because an electrostatic force appears between the LDH sheets, on the one hand, and the polar negative nitrogen and the oxygen functional groups, on the other. These LDH sheets react with functional groups containing rNGO sheets, leading to the local creation of a bridge by an Ni–N–C or O bonding, as confirmed by X-ray photoelectron spectroscopy. These defects and the dislocation in the $\text{rNGO/Au}^{\text{@}}\text{LaNi-LDH}$ might be created through the Au ions loaded by a galvanic exchange reaction with a low order oxidation number of Ni. The defective sites on the rNGO surface create active sites and enhance the wrapping reactivity in $\text{rNGO/Au}^{\text{@}}\text{LaNi-LDH}$. As a result, Au nanoparticles and LDH nanosheets are covered by the outer layers of the wrapped rNGO to be encapsulated among the sheets. Due to this encapsulation, three-dimensional structures also appear upon the galvanic exchange reaction.

3.2. Characterization of nitrogen-doped $\text{rGO/Au}^{\text{@}}\text{LaNi-LDH}$ and rGO/LaNi-LDH hybrid

The surface area of the synthesized materials of rGO/LaNi-LDH 7.0% w/w, rGO/LaNi-LDH 90% w/w, rNGO/LaNi-LDH 15.0% w/w, and $\text{rNGO/Au}^{\text{@}}\text{LaNi-LDH}$

15.0% w/w (Fig. 2A-D) were measured using the nitrogen adsorption-desorption isotherm via the DH method and the BJH method cumulative (Table 1). The surface area analysis was conducted under the following conditions: pressure tolerance: 0.100/0.100 (ads/des), outgas time: 5.0 h, outgas temperature: 100 C, bath temperature: 77.3 K, equilibrium time: 60/60 sec (ads/des), and equilibrium timeout: 240/240 s (ads/des). The nitrogen adsorption-desorption isotherm for rGO/LaNi-LDH 7.0% w/w, rGO/LaNi-LDH 90% w/w, and rNGO/LaNi-LDH 15.0% w/w exhibited the characteristics of the Langmuir isotherm, Type IV. The maximum specific surface area in the rNGO/LaNi-LDH 15% w/w was found to be much larger than those of rGO/LaNi-LDH 7.0% w/w, rGO/LaNi-LDH 90% w/w, and rNGO/Au[@]LaNi-LDH 15.0% w/w. The higher surface area of the rNGO/LaNi-LDH 15.0% w/w nanohybrid may be attributed to the nitrogen doped on the surface of the graphene oxide, which reduced the aggregation of the LDH sheets and the graphitic plate. The surface area of rNGO/Au[@]LaNi-LDH 15.0% w/w due to the galvanic exchange at the surface of LDH was found to be smaller than that of rNGO/LaNi-LDH 15.0% w/w. This is due to the reducing number of LDH plates at the surface of rNGO as a result of their being trapped at the scrolling and warping rNGO or nanorod. The galvanic exchange at the rNGO surface led to the filling of the mesoporous holes with Au nanoparticles; hence, another reason for the reduced specific surface area. Given the fact that surface area and pore-size are the two key factors in electrocatalytic activity, the results obtained verify the favorable applicability of the electrocatalysts produced for increasing accessible reaction sites. **"Here Figure 2"**

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) analyses were performed on the rNGO, rNGO/LaNi-LDH, and rNGO/ Au[@]LaNi-LDH hybrids to determine their features on a nanometer scale. Figure 3 (a and b) shows the TEM micrographs of the rNGO layers, indicating their thin and

transparent nature. There are some corrugations and scrollings in the graphene stacks resulting in a curled morphology. Figure 3 (c and d) shows the TEM images of the rNGO/LaNi-LDH synthesized hybrids using ultrasonic irradiation. However, the shape of the LaNi-LDHs particles is clearly observable at low magnification and there is clear evidence for the formation of LDHs nanosheets. Figure 3 (e–h) shows the HR-TEM and TEM of the rNGO/Au[@]LaNi-LDH hybrids. The presence of the intercalated LDH and Au nanoparticles at the edge of the rNGO effectively prevents the agglomeration and restacking of graphene sheets, which consequently helps maintain their high active surface area. The semi-nanorods also reveal that the rNGO/Au[@]LaNi-LDH 3D catalyst is curled and warped, which is favorable as it increases the accessible reaction sites. Due to the two-dimensional sheet-on-sheet structures of rNGO and LDH lacking agglomerated Au nanoparticles, a higher contact surface area with more linkage sites is offered in the rNGO/Au[@]LaNi-LDH structures. Au nanoparticles supported on the LDH and rNGO and/or rGO have positive effects, as a result of which the electrochemical performance of the modified nanoparticles is improved for the hydrogen evolution reaction.

"Here Figure 3"

The FT-IR spectra of GO, rGO/LaNi-LDH, and rNGO/LaNi-LDH hybrids are shown in Figure 4. The peaks at 3404 cm⁻¹ and 1363 cm⁻¹ in GO (Fig. 4a), those at 3310 cm⁻¹ and 1371 cm⁻¹ in rGO/LaNi-LDH (Fig. 4b), and the ones at 3325 cm⁻¹ and 1368 cm⁻¹ in rNGO/LaNi-LDH (Fig. 4c) are attributed to the O–H stretching and bending vibrations, and other oxygen-containing functional groups corresponding to epoxide/ether C–O–C and alkoxy or alkoxide C–OH situated at the edges of rNGO, respectively. The peak at 1605 cm⁻¹ (aromatic C=C) may be assigned to the skeletal vibrations of unoxidized graphitic domains for rGO (Fig. 4a). These main characteristic peaks indicate that rGO and rNGO/LaNi-LDH were synthesized successfully. A considerable change can also be

detected for rNGO/LaNi-LDH in the fingerprint region of the spectrum, showing the evolution of the bonding structure. Moreover, the broad peak appearing at $\approx 1046\text{ cm}^{-1}$ is probably due to the formation of N–C bonds and the residual C–O groups [31,32]. However, the FT–IR spectra of the LaNi-LDH part of the rGO/LaNi-LDH and rNGO/LaNi-LDH confirm the formation of a hydroxylated structure. Indeed, all the characteristic bands of the brucite-like metal hydroxide layers such as the vibration band of the O–H bonds and M–O/M–OH are observed [33,34]. **"Here Figure 4"**

X-ray photoelectron spectroscopy is an effective technique commonly used to gain a better understanding of the elemental composition and oxidation states of metal cations. In this study, the technique was employed to confirm the formation of Au nanoparticles and the presence of a nitrogen bridge ($\text{Au}^{\text{@}}\text{LaNi-LDH-N-C}$) between the LDH layers and the graphene sheets. $\text{Au}^{\text{@}}\text{LaNi-LDH-N-C}$ plays a pivotal role in improving the electrochemical performance of the rNGO/ $\text{Au}^{\text{@}}\text{LaNi-LDH}$ hybrid. The XPS spectrum of the rNGO/LaNi-LDH exhibits characteristic peaks corresponding to C 1s, O 1s, N 1s, Ni $2p_{3/2}$, Ni $2p_{5/2}$, La $3d_{3/2}$, and La $3d_{5/2}$ components while rNGO/ $\text{Au}^{\text{@}}\text{LaNi-LDH}$ exhibits all the peaks of rNGO/LaNi-LDH as well as those related to Au $4f_{7/2-5/2}$ (Figure 5).

"Here Figure 5"

The XPS spectra show a distinct evolution of nitrogen peak in all the nitrogen-doped hybrid samples, which is absent in the GO nanosheets. The deconvoluted high-resolution N 1s XPS spectrum of the rNGO/LaNi-LDH shows six different types of nitrogen configurations on the rNGO nanosheets (Fig. 5A, a₄), which include LaNi-LDH-N (392.88 eV and 396.3 eV), pyridinic-N (399.91 eV), pyrrolic-N (402.8 eV), graphitic-N (402.9 eV), N-oxide (405 eV), and nitrate-N (408.5 eV) [35–38]. Moreover, N 1s for rNGO/ $\text{Au}^{\text{@}}\text{LaNi-LDH}$ has the following five different peaks: $\text{Au}^{\text{@}}\text{LaNi-LDH-N}$ (390–396 eV), pyridinic-N (398.1 eV), pyrrolic-N (399.95 eV), graphitic-N (401.2 eV), and N-oxide

(402.8 eV). Pyridinic-N refers to the nitrogen atoms located at the edge of the graphene plate and bonded to two carbon atoms. It donates one π -electron to the aromatic π system. Pyrrolic-N refers to the nitrogen atoms bonded to two carbon atoms, which contribute to the π system with two π -electrons. The quaternary nitrogen is alternatively called “graphitic nitrogen” or “substituted nitrogen”, in which nitrogen atoms are incorporated into the graphene layer and replace carbon atoms within a graphene plane. The role of the real “electrocatalytically active sites” is still controversial since their contribution to the catalytic activity is not well established. In some studies, the enhanced electrocatalytic activity is attributed to pyridinic-N and/or pyrrolic-N. A recent study suggests that the graphitic nitrogen is more important for the electrocatalytic activity of the nitrogen-doped carbon [34,35,39]. The XPS results indicate that N-graphene contains all these four functional groups. The area of the nitrogen-metal connection is observed for the metals of LDH sheets from 390 to 400 eV, and they are the most important peaks among all the deconvoluted peaks contributing to the more effectively active sites for hydrogen evolution reaction [36,37].

The challenge of galvanic exchange is resolved by the analysis of the XPS spectrum of nickel at LDH sheets and determination of the oxidation state of Au. In the case of the rNGO/Au[@]LaNi-LDH, the XPS spectrum from Au 4f_{7/2-5/2} (Fig. 5B, b₃) exhibits one doublet peak (F₁ and F₂) for Au⁰ at (83.86–87.58 eV). This suggests that Au³⁺ ions are partially reduced to Au⁰ due to the electron transfer from the intercalated Ni metal of the rGO or rNGO/LDH sheets since the reduction of Au³⁺ is thermodynamically favorable. This agrees well with the significantly deconvoluted Ni 2p_{3/2} spectrum (Fig. 5A, a₃) [35,37,38]. For nickel in the LDH sheets, the spin-orbit splitting of the 2p_{3/2} and 2p_{1/2} is, in most cases, bordered enough; so, it only suffices to consider the more intense 2p_{3/2} signal. Fig. 5A, (a₃) presents the spectral fitting of the metal, oxide, and hydroxide spectral

components to XPS data measured for the rNGO/LaNi-LDH system containing all the three species (i.e., Ni metal, NiO, Ni hydroxide shown in black, blue, and red, respectively) [42].

The XPS of C 1s, ranging from 278 to 293 eV, is shown in Fig. 5 (a₁ and b₁). Generally, there are different types of the main C groups on rNGO/Au[@]LaNi-LDH and rNGO/LaNi-LDH, which are characterized by several spectral peaks such as C=C at 284.7 eV, C–OH at 285.4 eV, C=O at 286.5 eV, and C–C=O at 288.5 eV (Fig. 5, a₁ and b₁). As is well known, the C=O peak overlays that of C–N around a binding energy of 288.3±0.5 eV. The XPS spectra of O1s before and after the galvanic exchange are shown in Fig. 5 (a₂ and b₂, respectively), revealing C–OH at 534 eV, C=O at 533.2 eV, and C(O)OH at 531.5 eV as well as the OH at the surface of LDH at 529.5 eV [39,43,44]. The two typical peaks of La 3d_{3/2} and La 3d_{5/2} observed in Fig. 5 (b₄) are close to those expected for the La³⁺ ions from La(OH)₃ [40]. **"Here Figure 5"**

3.3. Electrochemical characterization of the prepared electrocatalysts

The electrochemical characterization of the rNGO/LaNi-LDH and rNGO/Au[@]LaNi-LDH modified GCEs were investigated in a 0.5 mol L⁻¹ H₂SO₄ solution. However, the electrochemical results are reported based on the relative standard deviation expressed in percent. These values are 21.8% and 0.9% for the exchange current density and voltage, respectively. The cyclic voltammetric responses of rNGO/LaNi-LDH and rNGO/Au@LaNi-LDH are shown in Fig. 6D (a and b, respectively). The peak appearing in the range of –0.50 to +1.50 V (vs. Ag/AgCl) belongs to Au, confirming that Au

successfully replaced for the Ni on the surface of rNGO/LaNi-LDH.

The electrocatalytic activities of the rNGO/Au@LaNi-LDH, rNGO/LaNi-LDH, rGO/Au@LaNi-LDH, and rGO/LaNi-LDH toward the hydrogen evolution reaction were evaluated using linear sweep voltammetry (LSV). For this purpose, the electrocatalytic activities of rGO/LaNi-LDH (7.0, 15.0, 30.0 and 90.0% w/w of LaNi-LDH to rGO) modified glassy carbon electrode toward the hydrogen evolution reaction were investigated in a 0.5 mol L⁻¹ H₂SO₄ solution (Fig. 6A). The results indicated that rGO/LaNi-LDH 90.0% w/w produces a higher current (Fig. 6A, d) with a lower overvoltage than the other rGO percentages (including 30.0, 15.0, and 7.0 w/w% LaNi-LDH to GO). Increasing the amount of rGO relative to that of LaNi-LDH was observed to improve the catalytic behavior of the nanocomposite since graphene took part as an ideal conductive surface. Moreover, rGO provides a greater surface area for the rGO/LaNi-LDH 90.0% w/w. Therefore, the much faster electron transfer and the actual surface area of the rGO/LaNi-LDH 90% w/w play the key factors contributing to the greatly enhanced catalytic activity toward the hydrogen evolution reaction. It must be noted that increasing the loading of rGO sheets also had a negative effect on the electrocatalytic activity of rGO/LaNi-LDH because the catalytic activities of (7.0, 15.0, and 30.0 w/w) rGO/LaNi-LDH were less than that of rGO/LaNi-LDH 90% w/w. This is due to the fact that the amount of LaNi-LDH serving as a real electrocatalyst decreases at a higher ratio of rGO, which leads to the reduced electrocatalytic activity. Thus, the rGO/LaNi-LDH 90.0% w/w was selected for further study.

In synthesizing rGO/Au@LaNi-LDH by the galvanic exchange reaction, it is important to determine the amount of Au loading on the surface of the rGO/LaNi-LDH [43,44]. Simultaneous with changes in the duration of the galvanic Au and Ni exchange, such parameters as gold nanoparticle size and morphology, the population of gold

nanoparticles, surface areas of graphene and LDH sheets, residual hydroxyl groups, and metal dispersion also change. A balanced combination of all these factors yields an optimal gold nanoparticles loading to achieve a high catalyst efficiency. Therefore, the effects of the exchange reaction time during the synthesis of Au[@]LaNi-LDH was investigated on the electrocatalytic activity of rGO/Au[@]LaNi-LDH in a solution of 0.5 mol L⁻¹ H₂SO₄. For this purpose, the rGO/LaNi-LDH-glassy carbon electrode was used for the galvanic exchange reaction over different durations (between 20 to 100 min) to prepare rGO/Au[@]LaNi-LDH. The products of the various reaction times were then compared for their electrochemical activities in the hydrogen evolution reaction. Results showed that the rGO/Au[@]LaNi-LDH prepared in 60 min had a higher electrocatalytic activity in the hydrogen evolution reaction.

In the second part of the study, a combination of rNGO and LDH was checked for the electrocatalyst behavior of the hybrid. For this propose, the electrocatalytic activity of rNGO/LaNi-LDH 15.0% w/w and rNGO/Au[@]LaNi-LDH 15.0% w/w (after their immobilization on the surface of a glassy carbon electrode) were evaluated. The linear sweep voltammograms of rNGO/LaNi-LDH and rNGO/Au[@]LaNi-LDH (15.0% w/w) in a 0.5 mol L⁻¹ H₂SO₄ solution were recorded (Fig. 6C, a and b) to find that while the current density and onset potential of the hydrogen evolution reaction improved. The current densities of rNGO/LaNi-LDH and rNGO/Au[@]LaNi-LDH were slightly lower, and the onset potentials were slightly higher than those of the commercial Pt-C. However, both rGO/Au[@]LaNi-LDH and rNGO/Au[@]LaNi-LDH showed better electrocatalytic activities (based on their current densities and onset potentials) than did rGO/LaNi-LDH or rNGO/LaNi-LDH (Figs. 6B and 6C). The interfacial covalent bonds between the metallic Au[@]LaNi-LDH and the nitrogen graphene layers also guarantee the strong molecular framework of the hybrid. Evidently, the critical role of the LDH nanosheets in inducing more positive charges from the Au[@]LaNi-LDH metals on nitrogen and the balanced

diameter size and population of the gold nanoparticles help H^+ adsorption by the chemical and electronic couplings, which ultimately produce an excellent electrocatalyst.

"Here Figure 6"

Tafel slope of an electrocatalyst is an inherent property that reveals the rate limiting step of the hydrogen evolution reaction. Tafel analysis distinguishes the possible mechanistic steps during the hydrogen generation at the surface of the electrocatalyst. In an acidic solution, the following three reaction steps are likely to occur in the generation of hydrogen at the surface of the electrocatalyst:

Based on previous reports [45,46], a Volmer-Tafel mechanism for the rate limiting step of the hydrogen evolution reaction suggests that the recombination step is a rate limiting one and that a Tafel slope of 30 mV per decade must be considered for the hydrogen evolution reaction. A Tafel slope of 40 mV per decade suggests hydrogen generation via the Volmer–Heyrovsky mechanism and the rate-limiting step in this case is of the electrochemical desorption type [43]. Finally, a Tafel slope of 120 mV per decade indicates that the mechanism might have arisen from various reaction pathways and that it depends on the surface coverage of the adsorbed hydrogen. The significant linear Tafel plots are fitted to the Tafel equation, $(\eta = b \cdot \log(j) + j_o)$, where j is the current density and b is the Tafel slope. This yields Tafel slopes of ~95.42, ~60, ~162, and ~88.3 mV per decade for rNGO/LaNi-LDH, rNGO/Au@LaNi-LDH, rGO/LaNi-LDH and rGO/Au@LaNi-LDH, respectively (Fig. 7). The hydrogen evolution activities of the proposed nanocomposites and several recently reported electrocatalysts are compared in Table 2. "Here Fig. 7"

Catalytic stability is another significant criterion for evaluating the hydrogen

evolution reaction. In this study, the following two methods were used for this purpose. First, the long-term stability of rNGO/Au[@]LaNi-LDH was investigated using continuum cyclic voltammetry (from 1 to 1000 cycles). Second, the electrocatalytic activity of rNGO/Au[@]LaNi-LDH was studied in acidic media at different times every 24 h (from 1 to 120 h) using a 0.5 mol L⁻¹ H₂SO₄ solution. The results showed that the current density increased but the overpotentials reduced (for the hydrogen evolution reaction) in the case of rNGO/Au[@]LaNi-LDH with increasing scan numbers from 1 to 1000 and from 0 to 120 h (Figs. 8A and 8B). The linear sweep voltammogram of rNGO/Au[@]LaNi-LDH was recorded in a 0.5 mol L⁻¹ H₂SO₄ solution to investigate the behavior of the electrocatalyst after 100 cycles and 24 h. The results obtained were confirmed by further increases in the porosity of the electrocatalyst from the 1st to the 1000th scan and/or from 24 to 120 h. The results confirm the stability of the electrocatalyst for the hydrogen evolution reaction.

"Here Figure 8"

4. Conclusion

LaNi-LDH nanoplates were synthesized in the rNGO and rGO environments. Au nanoparticles were then loaded on those nanoplates using a simple and inexpensive method comprising the galvanic exchange and sono-chemical reactions. The rNGO/Au[@]LaNi-LDH and rNGO/LaNi-LDH hybrids with highly exposed edges and excellent morphological changes during their galvanic exchange reaction turned into excellent electrocatalysts with a small Tafel slope. It was, therefore, concluded that the rNGO/Au[@]LaNi-LDH with an overpotential of -80 (mV vs. RHE) at an exchange current density of -10 (mA cm⁻²) is the best candidate among all the non-Pt electrocatalysts for the electrochemical hydrogen evolution reaction. The proposed approach of loading synthesized materials on graphene has led to the development of an advanced LDH

electrocatalyst with a highly competitive performance compared to the various hydrogen evolution electrocatalytic materials such as MoS_2 and WS_2 . Electrochemical studies showed that the gold nanoparticles synthesized via the galvanic exchange reaction had a perfect scale size to induce a satisfactory electroactivity for hydrogen evolution reaction. Undoubtedly, the porous materials (rGO and rNGO) with organic active sites, the presence of metal nanoparticles (Au), and the 2D spaces of the hydrotalcite materials (LaNi-LDH) are the key advantages for the enhanced hydrogen evolution in the proposed mechanism. Finally, improvement of the activity of $\text{rNGO/Au}^{\text{@}}\text{LaNi-LDH}$ prepared by the galvanic exchange reaction using other noble metals, and modification of the graphitic plate such doping phosphorus, sulfur, and born elements may be recommended for future research.

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References

- [1] Turner JA. Sustainable hydrogen production. *Science* 2004;305:972–4.
- [2] Rodríguez-Lugo RE, Trincado M, Vogt M, Tewes F, Santiso-Quinones G, Grützmacher H. A homogeneous transition metal complex for clean hydrogen production from methanol–water mixtures. *Nat Chem* 2013;5:342–7.
- [3] Hinnemann B, Moses PG, Bonde J, Jørgensen KP, Nielsen JH, Horch S, et al. Biomimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution. *J Am Chem Soc* 2005;127:5308–9.
- [4] Raoof J B, Hosseini R, Ojani R, Mandegarzarad S, MOF-derived Cu/nanoporous carbon composite and its application for electro-catalysis of hydrogen evolution reaction. *Energy* 2015;90:1075-81.
- [5] Sequeira CAC, Santos DMF, Brito PSD, Electrocatalytic activity of simple and modified Fe–P electrodeposits for hydrogen evolution from alkaline media. *Energy* 2011;36:847–53.
- [6] Liang J, Gao LJ, Miao NN, Chai YJ, Wang N, Song XQ, Hydrogen generation by reaction of Al–M (M = Fe,Co,Ni) with water. *Energy* 2016;113:282-287.
- [7] Jiang P, Liu Q, Ge C, Cui W, Pu Z, Asiri AM, et al. CoP nanostructures with different morphologies: synthesis, characterization and a study of their electrocatalytic performance toward the hydrogen evolution reaction. *J Mater Chem A* 2014;2:14634–40.
- [8] Wu L, He Y, Lei T, Nan B, Xu N, Zou J, Huang B, Liu C.T, Characterization of the porous Ni₃Al–Mo electrodes during hydrogen generation from alkaline water electrolysis. *Energy* 2013;63: 216–24.
- [9] Buurmans ILC, Ruiz-Martínez J, Knowles W V, van der Beek D, Bergwerff JA, Vogt ETC, et al. Catalytic activity in individual cracking catalyst particles imaged

503 throughout different life stages by selective staining. *Nat Chem* 2011;3:862–7.

504 [10] Oh TH, A formic acid hydrogen generator using Pd/C₃N₄ catalyst for mobile proton
 505 exchange membrane fuel cell systems. *Energy* 2016;112:679–685.

506 [11] He D, Jiang Y, Lv H, Pan M, Mu S. Nitrogen-doped reduced graphene oxide supports
 507 for noble metal catalysts with greatly enhanced activity and stability. *Appl Catal B Environ* 2013;132–133:379–88.

508

509 [12] Li X, Wang Z, Zhang J, Xie C, Li B, Wang R, et al. Carbon nanotube hybrids with
 510 MoS₂ and WS₂ synthesized with control of crystal structure and morphology. *Carbon*
 511 2015;85:168–75.

512 [13] Wu Z, Fang B, Bonakdarpour A, Sun A, Wilkinson DP, Wang D. WS₂ nanosheets as a
 513 highly efficient electrocatalyst for hydrogen evolution reaction. *Appl Catal B Environ*
 514 2012;125:59–66.

515 [14] Lin T-W, Liu C-J, Lin J-Y. Facile synthesis of MoS₃/carbon nanotube nanocomposite
 516 with high catalytic activity toward hydrogen evolution reaction. *Appl Catal B Environ*
 517 2013;134:75–82.

518 [15] Jaramillo TF, Jørgensen KP, Bonde J, Nielsen JH, Hørch S, Chorkendorff I.
 519 Identification of active edge sites for electrochemical H₂ evolution from MoS₂
 520 nanocatalysts. *Science* 2007;317:100–2.

521 [16] Tenne R, Margulis L, Genut Mea1, Hodes G. Polyhedral and cylindrical structures of
 522 tungsten disulphide. *Nature* 1992;360:444–6.

523 [17] Morales-Guio CG, Hu X. Amorphous molybdenum sulfides as hydrogen evolution
 524 catalysts. *Acc Chem Res* 2014;47:2671–81.

525 [18] Wang H, Tsai C, Kong D, Chan K, Abild-Pedersen F, Nørskov JK, et al. Transition-
 526 metal doped edge sites in vertically aligned MoS₂ catalysts for enhanced hydrogen
 527 evolution. *Nano Res* 2014;8:566–75.

- 528 [19] Zhang Y, Shi J, Han G, Li M, Ji Q, Ma D, et al. Chemical vapor deposition of
529 monolayer WS₂ nanosheets on Au foils toward direct application in hydrogen
530 evolution. *Nano Res* 2015;8:2881–90.
- 531 [20] Liu Q, Wu F, Cao F, Chen L, Xie X, Wang W, et al. A multijunction of ZnIn₂S₄
532 nanosheet/TiO₂ film/Si nanowire for significant performance enhancement of water
533 splitting. *Nano Res* 2015:1–11.
- 534 [21] Fan G, Li F, Evans DG, Duan X. Catalytic applications of layered double hydroxides:
535 recent advances and perspectives. *Chem Soc Rev* 2014;43:7040–66.
- 536 [22] Gomes JF, Puna JF, Gonçalves LM, Bordado JC. Study on the use of MgAl
537 hydrotalcites as solid heterogeneous catalysts for biodiesel production. *Energy* 2011;
538 12:6770-8.
- 539 [23] Dias AP, Bernardo J, Felizardo P, Correia MJ. Biodiesel production over thermal
540 activated cerium modified Mg-Al hydrotalcites. *Energy* 2012;1:344-53.
- 541 [24] Ma Y, Wang Q, Zheng L, Gao Z, Wang Q, Ma Y. Mixed methanol/ethanol on
542 transesterification of waste cooking oil using Mg/Al hydrotalcite catalyst. *Energy*
543 2016;107:523-31.
- 544 [25] Sławiński G. W., Ivanova O S., Zamborini F. P. Twin Plane Decoration of Silver
545 Nanorods with Palladium by Galvanic Exchange at a Controlled Rate. *Langmuir* 2011;
546 27: 13293-13301.
- 547 [26] Sun Y, Wiley B, Li ZY, Xia Y. Synthesis and optical properties of nanorattles and
548 multiple-walled nanoshells/nanotubes made of metal alloys. *J Am Chem Soc*
549 2004;126:9399-406.
- 550 [27] Bansal V, Jani H, Du Plessis J, Coloe PJ, Bhargava SK. Galvanic Replacement
551 reaction on metal films: A one-step approach to create nanoporous surfaces for
552 catalysis. *Adv Mater* 2008;20:717-23.

- 553 [28] Bi Y, Lu G. Facile synthesis of platinum nanofiber/nanotube junction structures at room
554 temperature. *Chem Mater* 2008;20:1224-6.
- 555 [29] Selvakannan PR, Sastry M. Hollow gold and platinum nanoparticles by a
556 transmetallation reaction in an organic solution. *Chemical communications* 2005;1684-
557 6.
- 558 [30] Hummers Jr WS, Offeman RE. Preparation of graphitic oxide. *J Am Chem Soc*
559 1958;80:1339.
- 560 [31] Lai L, Chen L, Zhan D, Sun L, Liu J, Lim SH, Poh CK, Shen Z, Lin J. One-step
561 synthesis of NH₂-graphene from in situ graphene-oxide reduction and its improved
562 electrochemical properties. *Carbon* 2011;49:3250-7.
- 563 [32] Shin HJ, Kim KK, Benayad A, Yoon SM, Park HK, Jung IS, Jin MH, Jeong HK, Kim
564 JM, Choi JY, Lee YH. Efficient reduction of graphite oxide by sodium borohydride and
565 its effect on electrical conductance. *Advanced Functional Materials* 2009;19:1987-92.
- 566 [33] Rezaei B, Khosropour H, Ensafi AA, Dinari M, Nabiyan A. A new electrochemical
567 sensor for the simultaneous determination of guanine and adenine: using a NiAl-
568 layered double hydroxide/graphene oxide-multi wall carbon nanotube modified glassy
569 carbon electrode. *RSC Adv* 2015;5:75756–65.
- 570 [34] Ensafi AA, Jafari-Asl M, Nabiyan A, Rezaei B, Dinari M. Hydrogen storage in hybrid
571 of layered double hydroxides/reduced graphene oxide using spillover mechanism.
572 *Energy* 2016;99:103-14.
- 573 [35] Uchida T, Mogami H, Yamakata A, Sasaki Y, Osawa M. Hydrogen evolution reaction
574 catalyzed by proton-coupled redox cycle of 4, 4'-bipyridine monolayer adsorbed on
575 silver electrodes. *J Am Chem Soc* 2008;130:10862–3.
- 576 [36] Benayad A, Shin H-J, Park HK, Yoon S-M, Kim KK, Jin MH, et al. Controlling work
577 function of reduced graphite oxide with Au-ion concentration. *Chem Phys Lett*

578 2009;475:91–5.

579 [37] Yoon S-M, Kim UJ, Benayad A, Lee IH, Son H, Shin H-J, et al. Thermal conversion of
 580 electronic and electrical properties of AuCl₃-Doped single-walled carbon nanotubes.
 581 ACS Nano 2011;5:1353–9.

582 [38] Biesinger MC, Payne BP, Lau LWM, Gerson A, Smart RSC. X-ray photoelectron
 583 spectroscopic chemical state quantification of mixed nickel metal, oxide and hydroxide
 584 systems. Surf Interface Anal 2009;41:324–32.

585 [39] Wang Y, Shao Y, Matson DW, Li J, Lin Y. Nitrogen-doped graphene and its application
 586 in electrochemical biosensing. ACS Nano 2010;4:1790–8.

587 [40] Mota N, Alvarez-Galván MC, Navarro RM, Al-Zahrani SM, Goguet A, Daly H, et al.
 588 Insights on the role of Ru substitution in the properties of LaCoO₃-based oxides as
 589 catalysts precursors for the oxidative reforming of diesel fuel. Appl Catal B Environ
 590 2012;113:271–80.

591 [41] Mondal S, Johnston JM, Wang H, Khelashvili G, Filizola M, Weinstein H. Membrane
 592 driven spatial organization of GPCRs. Sci Rep 2013;3:1-9

593 [42] Murov SL, Carmichael I, Hug GL. Handbook of photochemistry. CRC Press; 1993.

594 [43] Malitesta C, Losito I, Sabbatini L, Zambonin PG. New findings on polypyrrole
 595 chemical structure by XPS coupled to chemical derivatization labelling. J Electron
 596 Spectroscopy and Related Phenomena 1995;76:629-34.

597 [44] Niwa Y, Kobayashi H, Tsuchiya T. X-ray photoelectron spectroscopy of
 598 tetraphenylporphin and phthalocyanine. J Chem Phys 1974;3:799-807.

599 [45] Ensafi AA, Jafari-Asl M, Rezaei B. Graphene/nano-porous silicon and
 600 graphene/bimetallic silicon nanostructures (Pt–M, M: Pd, Ru, Rh), efficient
 601 electrocatalysts for the hydrogen evolution reaction. Phys Chem Chem Phys
 602 2015;17:23770–82.

- [46] Ensafi AA, Jafari-Asl M, Nabiyan A, Rezaei B. Preparation of three-dimensional ruthenium oxide@graphene oxide based on etching of Ni-Al/layered double hydroxides: application for electrochemical hydrogen generation. *J Electrochem Soc* 2016;7: H610-7.
- [47] Dinari M, Nabiyan A, Ensafi AA, Jafari-Asl M. Polybenzimidazole and polybenzimidazole/MoS₂ hybrids as an active nitrogen sites: hydrogen generation application. *RSC Advance* 2015;5:100996-1005.
- [48] Huang Y, Miao Y-E, Zhang L, Tjiu WW, Pan J, Liu T. Synthesis of few-layer MoS₂ nanosheet-coated electrospun SnO₂ nanotube heterostructures for enhanced hydrogen evolution reaction. *Nanoscale* 2014;00:1–7.
- [49] Ji S, Yang Z, Zhang C, Liu Z, Tjiu WW, Phang IY, et al. Exfoliated MoS₂ nanosheets as efficient catalysts for electrochemical hydrogen evolution. *Electrochim Acta* 2013;109:269–75.
- [50] Wang D-Y, Gong M, Chou H-L, Pan C-J, Chen H-A, Wu Y, et al. Highly active and stable hybrid catalyst of cobalt-doped FeS₂ nanosheets–carbon nanotubes for hydrogen evolution reaction. *J Am Chem Soc* 2015;137:1587–92.
- [51] Chhetri M, Gupta U, Yadgarov L, Rosentsveig R, Tenne R, Rao CNR. Beneficial effect of Re doping on the electrochemical HER activity of MoS₂ fullerenes. *Dalt Trans* 2015;44:16399–404.
- [52] Tang H, Dou K, Kaun C-C, Kuang Q, Yang S. MoSe₂ nanosheets and their graphene hybrids: synthesis, characterization and hydrogen evolution reaction studies. *J Mater Chem A* 2014;2:360–4.

Table 1. The surfaces area, pore volumes and pore sizes of the difference electrocatalysts.

BJH method cumulative			
Catalyst	Surface area	Pore volume	Pore size
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)
7% w/w rGO/LaNi-LDH	164	0.22	4.64
90% w/w rGO/LaNi-LDH	309	0.40	4.57
15% w/w rNGO/LaNi-LDH	493	0.66	4.57
15% w/w rNGO/Au [@] LaNiLDH	316	0.44	2.46
DH method			
Catalyst	Surface area	Pore volume	Pore size
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)
7% w/w rGO/LaNi-LDH	169	0.22	4.64
90% w/w rGO/LaNi-LDH	317	0.40	4.57
15% w/w rNGO/LaNi-LDH	500	0.66	4.57
15% w/w rNGO/Au [@] LaNiLDH	329	0.44	2.46

649 **Table 2.** Collected HER catalysis data.

Catalyst	Overpotential (mV vs. RHE)	Exchange current density (mA cm ⁻²)	Tafel slope (mV decade ⁻¹)	Reference
Polybenzimidazole-MoS ₂	160	-10	50.6	47
MoS ₂ /SnO ₂	-187	-10	59	48
Exfoliated MoS ₂	>-500	-10	70	49
FeS ₂ /CNT	-120	-20	46	50
Re doped MoS ₂	~-260	-10	136	51
MoSe ₂ /rGO	-115	-10	69	52
rGO/Au [@] LaNi-LDH	-145	-10	88.3	This work
rNGO/Au [@] LaNi-LDH	-80	-10	60	This work

All electrochemical data were collected in H₂SO₄ 0.5 mol L⁻¹.

Legends for the figures:

Fig. 1. Synthesis of rNGO/Au[@]LaNi-LDH by hydrothermal and sonochemical methods.

Fig. 2. N₂ adsorption/desorption isotherm of (A): 7.0% w/w rGO/LaNi-LDH, (B): 15.0% w/w rNGO/LaNi-LDH, (C): 15.0% w/w rNGO/Au[@]LaNi-LDH, and (D) 90% w/w rGO/LaNi-LDH.

Fig. 3. TEM and HR-TEM images of (a and b): rNGO, (c and d): rNGO/LaNi-LDH, and (e-h): rNGO/Au[@]LaNi-LDH.

Fig. 4. FT-IR spectra of (A): rGO, (B): rGO/LaNi-LDH, and (C): rNGO/LaNi-LDH.

Fig. 5. XPS analysis of rNGO/LaNi-LDH and rNGO/Au[@]LaNi-LDH (A): before galvanic exchange (a₁) C 1s, (a₂) O 1s, (a₃) Ni 2p, and (a₄) N 1s; and (B): after galvanic exchange (b₁) C 1s, (b₂) O 1s, (b₃) Au 4f, and (b₄) La 3d.

Fig. 6. Linear sweep voltammograms for hydrogen evolution reaction in 0.5 mol L⁻¹ H₂SO₄ at (A): (a): 7.0% w/w rGO/LaNi-LDH, (b): 15.0% w/w rGO/LaNi-LDH, (c): 30.0% w/w rGO/LaNi-LDH, and (d) 90% w/w rGO/LaNi-LDH. (B): Linear sweep voltammograms of (a): rGO/LaNi-LDH, and (b): rNGO/LaNi-LDH in 0.5 mol L⁻¹ H₂SO₄. (C): Linear sweep voltammograms of (a): rNGO/Au[@]LaNi-LDH, and (b): rGO/Au[@]LaNi-LDH in 0.5 mol L⁻¹ H₂SO₄. (D): Cyclic voltammograms of (a): rGO/ LaNi-LDH, and (b): rGO/Au[@]LaNi-LDH in 0.5 mol L⁻¹ H₂SO₄. All the currents are normalized based on the BET results.

Fig. 7. Tafel plots of (a): rGO/LaNi-LDH, (b): rGO/Au[@]LaNi-LDH, (c): rNGO/LaNi-LDH, and (d) rNGO/Au[@]LaNi-LDH, in 0.5 mol L⁻¹ H₂SO₄.

Fig. 8. Linear sweep voltammograms for long-term electrochemical stability test of rNGO/Au[@]LaNi-LDH; (A): 1th to 1000th cycles with a scan rate of 20 mV s⁻¹, and (B)

687 from 1 h, to 120 h in 0.5 mol L⁻¹ H₂SO₄, with a scan rate of 20 mV s⁻¹. All the currents are
688 normalized based on the BET results.

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8