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Coaxial nanofibers of nickel/ gadolinium oxide /nickel oxide as highly effective electrocatalysts for hydrogen evolution reaction

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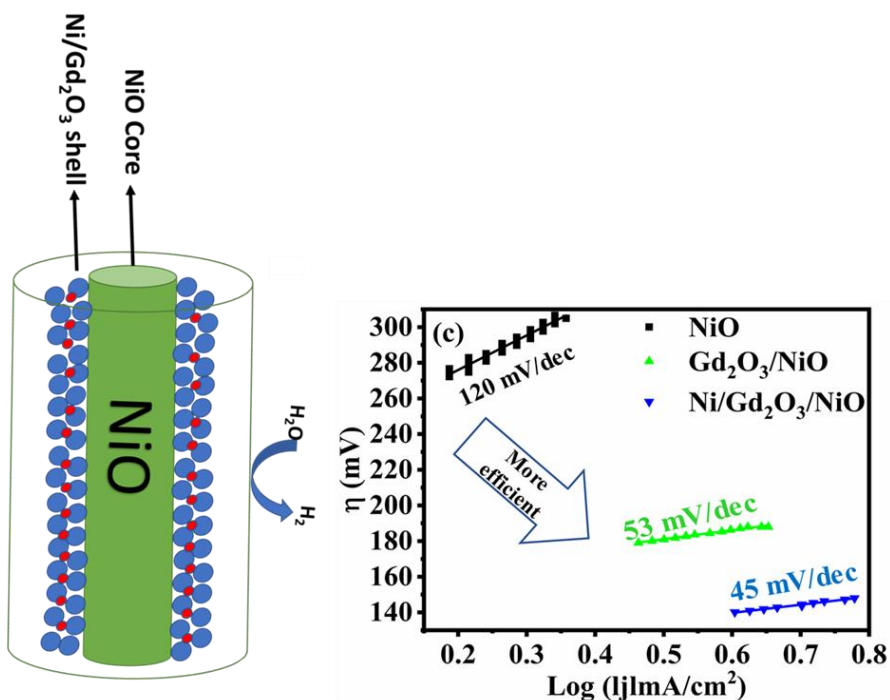
Abstract

Cost-effective, active and stable electrocatalysts are pivotal to hydrogen production via electrocatalytic water splitting. Here we report on the preparation of novel nanofiber (NF) Ni/Gd₂O₃/NiO heterostructures by an electrospinning technique. The fabricated materials show high electrocatalytic performance for hydrogen evolution reaction (HER) with activities of onset potential at 89 mV, which is almost identical to that of platinum. The chemical and electronic properties of materials are successfully optimized in Ni/Gd₂O₃/NiO coaxial heterostructures; the NiO NF with Gd³⁺ enhances remarkably its electrical conductivity and promotes HER reaction kinetics. It offers the distinct advantages of long-term durability and readiness for the integration into producing hydrogen via HER, affording better performance than benchmark Pt catalysts. The

successful fabrication of these metal oxides nanofibers and nanostructures may pave a new path for rational synthesis of efficient HER catalysts.

Key words: HER, Coaxial nanofibers, Ni/Gd₂O₃/NiO, Hydrogen generation, and water splitting.

Graphical Abstract:



Highlights:

- Elaborated NiO nanofibers decorated with Ni/Gd₂O₃ as coaxial structure.
- The Ni/Gd₂O₃/NiO has onset potential better than platinum electrode during the measurement of HER.
- The Ni/Gd₂O₃/NiO coaxial nanofibers have long-term durability during hydrogen generation.
- The highest exchange current density of Ni/Gd₂O₃/NiO up to 1.85 mA/cm² compared to most noble metal-free catalysis with decay of charge transfer resistance.

1. Introduction

In recent years, nickel oxide has been intensively studied for numerous applications, such as electrocatalysts [1-3], electrochemical capacitance [4-7] and for energy production [8]. All of that is mainly due to its particular properties as chemical, physical, specific electrochromic, thermoelectric and supercapacitance. Nickel oxide can be used in advanced technologies depending on its synthesis conditions and microstructures [9-16]. Many routes have been successfully applied to fabricate different NiO morphologies, including precipitation methods [17], hydrothermal [18, 19], solvothermal [20, 21], microemulsion [22, 23], oxidation of metallic Ni [24], thermal decomposition of Ni(II)- metalloorganic [25] and electrospinning [26-31].

Among these methods, the electrospinning has turned out to be a preferable choice because of its simplicity and scalability to yield nanofibers at an industrial level, and easy control over the morphology of the nanofibers [32-40]. Nickel oxide nanofiber morphology has gained significant attention due to the strong dependence of properties on the morphology [28, 41, 42]. The 1D nanofibers are easily modified *via* various approaches such as doping with heteroatoms, introducing strain in the basal plane, synergizing with conductive materials, coupling with the substrates of more active sites and defects to enhance the electrical conductivity and accelerating the kinetics of charge transfer [43-45]. These modification approaches could also be used to enhance the electrocatalytic performance of NiO NF as an ideal catalyst for energy production and, in specific, for the hydrogen evolution reaction (HER) *via* electrocatalytic water splitting [46]. One of the most significant challenges is the discovery of renewable, clean, safe, and sustainable energy sources to handle the expected shortage of non-renewable energies while controlling pollution. Hydrogen is a clean, zero carbon emission fuel when burned in oxygen. It is a promising approach as a renewable fuel for spacecraft, aircraft, vehicles, propulsion, and electric devices. Electrochemical water splitting is an effective and easy way of generating high-purity hydrogen. The most common HER electrocatalysts are using Pt metal with a high exchange current density and a near-zero overpotential [47]. However, Pt has many disadvantages like scarcity of supply, high cost, susceptibility to poisoning and a lack of durability of the catalyst. Despite the good electrocatalytic properties of Ni-based nanomaterials and nanofibers, few works in recent years have been conducted towards using these materials as alternative electrocatalysts for HER instead of Pt. For example, C@NiO/Ni nanofibers, prepared by electrospinning and a subsequent carbonization process, showed high effective and stable electrocatalytic for HER up to 22 hours

[48]. NiO and CrO₃ double surface-decorated Ni (Ni@ NiO@CrO₃) nanofibers showed good electrocatalytic activity (100 mA cm⁻² at a low overpotential versus RHE at 228 mV) and superior stability (more than 120 h without decay) [49]. Yan and co-workers [50] reported an HER current of 5 mA cm⁻² at an overpotential of 110 mV with good stability for crystalline/amorphous core/shell Ni/NiO nanosheets. The good electrocatalytic activity of these nanosheets has been explained by the good conductivity of Ni nanoparticles on the surface of the fibers [49, 50]. Similarly, the embedding of Gd₂O₃ and Gd particles was shown to enhance the electrocatalytic activity of Ni-Co alloy and Ni-CeO₂-Gd electrodes to HER, respectively [51, 52]. Recently, we prepared self-supported carbon-Ni/NiO-Pd nanofiber electrodes for hydrogen and oxygen evolution reactions [53].

In the present work, we elaborate a novel Ni/Gd₂O₃/NiO coaxial heterostructures by an electrospinning technique. According to the best of our knowledge, no reports on such heterostructures for HER applications have been described so far. The nano-interfaces at Ni/NiO heterostructure is expected to enhance HER by stabilizing hydrogen atoms on metallic Ni and releasing the generated OH⁻ on NiO site [2]. Moreover, the metallic Ni on the surface of the nanofibers facilitates the electron transfer. However, NiO/Ni heterostructures are not stable and exhibited high decay over time. Here, inspired by the fact that the addition of Gd₂O₃ to Ni-based materials could increase their corrosion resistance and stability [54], we introduced Gd₂O₃ to enhance the stability of Ni/NiO heterostructure. Moreover, the interaction between Gd₂O₃ and NiO might generate new catalytic sites by alloying at the interfaces [55]. The fabricated electrocatalyst exhibits high electrocatalytic performance for hydrogen evolution reaction (HER) with activities of onset potential at 89 mV, which is almost identical to that of platinum. Moreover, Ni/Gd₂O₃/NiO offers the advantages of long-term durability after an accelerated scan of 5000 cycles as well as ready integration into an electrolyzes for HER, affording better performance than benchmark Pt catalysts.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade and used as received without further treatment. Nickel acetate (Ni(CH₃COO)₂·4H₂O, 98%), gadolinium nitrate (Gd(NO₃)₃·6H₂O, 99.9%), ethanol

(99.8%), dimethylformamide (DMF, 99.8%), poly(vinylpyrrolidone) (PVP, molecular weight 1300 000), isopropanol (98%), potassium hydroxide (KOH \geq 85%) and 5 wt% NAFION solution were purchased from Sigma-Aldrich.

2.2.Preparation of nanofibers

In a typical procedure, 0.5 g of nickel acetate tetrahydrate and 0.0477 g of gadolinium nitrate hexahydrate were dissolved in a solvent mixture of 2mL DMF and 2 mL ethanol with overnight stirring (precursor solution) to obtain the Ni:Gd = 2.009:0.106 mole ratio. 0.5 g of PVP dispersed in 4 mL ethanol by stirring overnight was then added to the precursor solution. Nanofibers were spun in a home-built electrospinning apparatus at an electric potential of 25 kV with a feed rate of 2mL/ h from the obtained solution. Nanofibers were picked on a rotating coil covered with an aluminium foil with a rotation speed of 400 rpm for 15 cm from the syringe tip. The composite nanofibers were collected and calcined in a muffle furnace at 600 °C, with a heating rate of 1 °C/min, for 3 h under air or Ar atmosphere. In the following, the prepared nanofibers without Gd₂O₃ are labelled as NiO, while the doped NiO nanofibers with 5 at% Gd then it has been calcined in different gases; air and Ar are denoted as Gd₂O₃/NiO and Ni/Gd₂O₃/NiO, respectively.

2.3.Characterization of nanofibers

The phase composition of the materials was analyzed by X-ray diffraction (XRD), using a PANalytical Xpert-PRO diffractometer equipped with an Xcelerator detector using Ni-filtered Cu radiation (CuK α 1 radiation wavelength 0.1540598 nm and CuK α 2 radiation wavelength 0.1544426 nm) at 40 kV and 40 mA. In order to obtain XRD patterns with good quality, the nanofibers were well ground, and the obtained powder samples were scanned at a scanning rate of 0.1° min⁻¹ (i.e., step size and time of 0.02° and 12 seconds, respectively) in the 2 θ range of 10–90°. Rietveld refinement was performed using the FULLPROF program [56] with profile function 7 (Thompson-Cox-Hastings pseudo-Voigt convoluted with an axial divergence asymmetry function) [57]. The resolution function of the instrument was obtained from the structure refinement of a silicon standard. Raman spectra were measured on a Horiba XploRA using a diode lasers by Cobolt laser (λ = 638 nm) at a power of 10 mW and an objective microscope lens of 100x.

The morphology and structure of the obtained nanofibers were observed by scanning electron microscopy (SEM) (Hitachi S4800, Japan). Energy-dispersive X-ray spectroscopy analysis (EDX) with elemental mapping was performed with a Zeiss EVO HD15 microscope coupled to an Oxford X-MaxN EDX detector. The fiber morphology was examined also using high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100, Japan) equipped with energy-dispersive X-ray (EDX) spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed using an Escalab 250 (Thermo Fisher Scientific, USA) using monochromatic Al K α (1486.6 eV) radiation at 2kV and 1 μ A. The surface diameter of 400 μ m was analyzed during the acquisition time of 1203.5 s for obtaining the elemental composition. Room-temperature continuous-wave (cw) electron paramagnetic resonance (EPR) measurements at X-band frequencies (9.78 GHz) were conducted with a Bruker B-ER420 spectrometer upgraded with a Bruker ECS 041XG microwave bridge and a lock-in amplifier (Bruker ER023M) using a Bruker TE102 resonator applying a modulation amplitude of 5 G and a modulation frequency of 100 kHz. The samples were measured in quartz tubes of 2.9 mm outer diameter. The elemental concentration in the nanofibers was detected using atomic absorption spectroscopy (AAS) (AAAnalyst 400, PerkinElmer). About 0.2 g of each nanofibers was annealed at 600 $^{\circ}$ C under air atmosphere for 6 h, and the obtained ash was dissolved in 2 mL of concentrated HNO $_3$ for 24 hrs. Then, the obtained solution was diluted in 0.2 L of water and used to detect Ni and Gd concentration by AAS.

2.4 Electrochemical measurements

The electrochemical tests were carried out by a Solartron SI 1287 galvanostatic-potentiostat in a three-electrode configuration with a platinum counter-electrode and a Ag/AgCl reference electrode (0.197 V vs. RHE at room temperature) in the presence of NAFION membrane (proton exchange membrane) to separate between the anode and cathode. During this measurement, 5 mg of prepared nanofibers were mixed with 1 mL of isopropanol and 40 μ l of NAFION solution by at least 15 min ultrasonication to form a homogeneous catalyst ink. Afterwards, 20 μ l of the ink was drop-casted on to a glassy carbon electrode of 3 mm diameter, dried and used as a working electrode. A Pt wire (CH-instrument, USA) was used on the cathode side as a standard material for comparison. The linear sweep voltammetry (LSV) curves were collected for HER at a potential scan rate of 5mV/s. The cyclic voltammograms (CV) were recorded in the potential range of 0.1 V to 0.3 V at a several scan rate of 10:100 mV/s. All electrochemical experiments were carried out at room temperature

and at ambient pressure in 1 M KOH as an electrolyte. The electrochemical impedance spectroscopy (EIS) was performed at 0.2 V vs. RHE in a frequency range of 0.1Hz to 1MHz with a voltage bias of 10 mV amplitude. Hydrogen measurements were recorded using gas chromatography (GC; Clarus-400, Perkin Elmer, TCD 2m*1mm and He as carrier gas).

3. Results and discussion

The NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO NFs were fabricated via electrospinning of polymeric solution containing nickel acetate and gadolinium nitrate as precursors. The XRD patterns of prepared NiO, Gd₂O₃/NiO and Ni/Gd₂O₃/NiO nanofibers were illustrated in Fig. 1. All XRD reflections observed in the pattern of NiO nanofiber can be assigned to the cubic NiO phase (space group *Fm-3m*, JCPDS card no. 01-75-0269) [58]. No additional reflections are observed, which could be attributed to impurities. we focussed on a narrower 2 Θ window for closer analysis in Fig 1b. By careful comparison of the observed peaks for each phase with those calculated from the respective reference structures of NiO (PDF #047-1049), Gd₂O₃ (PDF #012-0797) and metallic Ni (PDF #004-0850), we can clearly see the peaks corresponding to the (222), (400) and (440) planes of Gd₂O₃ phase at 2 θ of 28.6°, 33.14° and 47.57° and the (111) and (200) planes of NiO phase at 37.29° and 43.32°, as well as the (111) and (200) planes of Ni phase at 44.53° and 51.89°. Rietveld refinement of the XRD pattern of NiO nanofibers revealed that the sample is composed of nanocrystallites with a mean size of 27.3±0.7 nm and with a small microstrain of 1.63 x 10⁻⁴. The lattice parameter *a* of NiO phase in this sample was found to be 4.1762(2) Å, which is in good agreement with a previously reported value [58]. On the other hand, the NiO phase in the Gd₂O₃/NiO sample doped with 5 at% of Gd and calcined in air showed a slight increase in the lattice parameter in comparison with that of pure NiO nanofiber. This increase in the lattice parameter can be explained the substitution of larger Gd³⁺ for smaller Ni²⁺ cations in the NiO lattice [*r* (Gd³⁺) = 93.8 pm, *r* (Ni²⁺) = 69 pm; both ions are 6-fold coordinated [59]. A very small amount of nanocrystalline Gd₂O₃ (1.4(4) wt%) is observed as a side phase, suggesting that the fraction of Gd³⁺ in the NiO lattice is less than 5 at%. The calcination of the Ni/Gd₂O₃/NiO sample doped with 5 at% of Gd in argon atmosphere led to an increase in the amount of Gd₂O₃ phase combined with the segregation of 2.3(3) wt% of metallic Ni. It has been reported that transition elements can be reduced during the thermal decomposition of organic carbon based-materials such as acetate or PVP materials in Ar atmosphere [60, 61]. Moreover, the lattice parameter of NiO

phase in this sample is quite similar to that of pure NiO nanofiber, confirming the segregation of Gd_2O_3 from the NiO lattice during the calcination in Ar atmosphere. The lattice parameters of NiO, weight fractions, crystallite size, and microstructure of all samples as obtained by Rietveld refinement are listed in Table 1. As shown in Table 1, the crystallite size of NiO phase decreases with the addition of Gd dopant, which is consistent with the decrease in the size of NiO fibers as revealed by SEM characterizations (Fig. 2). The lower microstrain of NiO phase in the Ni/ Gd_2O_3 /NiO sample in comparison with that in Gd_2O_3 /NiO sample is due to the segregation of Gd^{3+} and Ni^{2+} from NiO lattice by calcination in Ar atmosphere.

Raman scattering is a useful technique to study the defect and distortion of the crystalline lattices. The Raman spectra of the synthesized nanofibers are illustrated in Figure S1. The broad peak observed at 510 cm^{-1} in the Raman spectra of all samples can be attributed to the Ni–O [53]. This peak is shifted to lower wavenumber for Gd_2O_3 /NiO nanofibers if compared with those of the other two samples. This shift can be explained by the increase in the unit cell volume of NiO phase in Gd_2O_3 /NiO nanofibers due to the substitution of Ni^{2+} by Gd^{3+} , as confirmed by XRD characterizations. The increase in cell volume is accompanied by an increase in the bond distances, thus, a decrease in the force constant and the corresponding wavenumber [62]. Moreover, the peak observed at $\sim 355\text{ cm}^{-1}$ in the Raman spectrum of Ni/ Gd_2O_3 /NiO sample can be assigned to the Gd_2O_3 phase [63]. These results are in good agreement with XRD results [63].

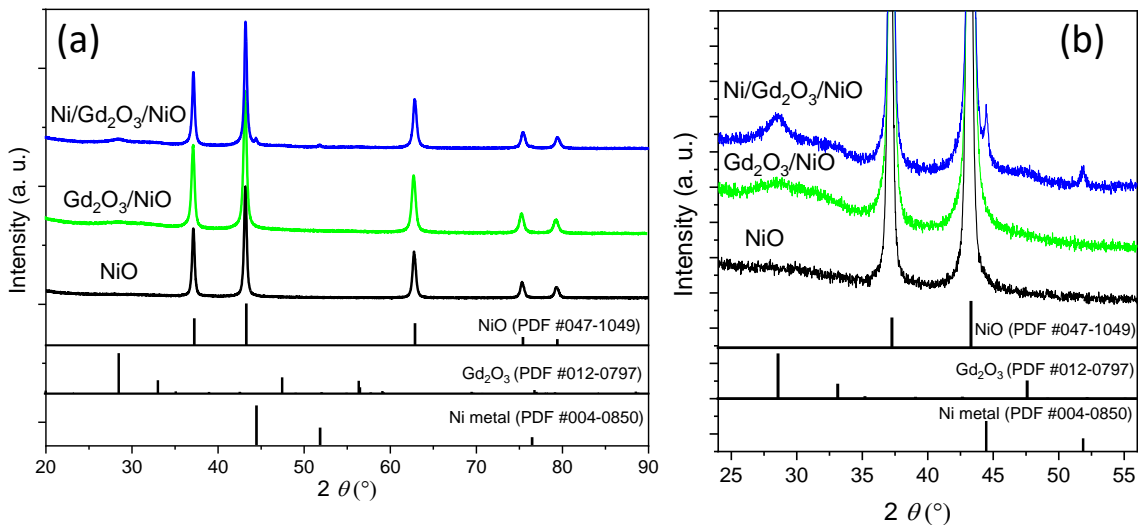


Fig. 1: XRD patterns of prepared NiO, Gd_2O_3 /NiO, and Ni/ Gd_2O_3 /NiO nanofibers. Panels b focusses on a narrower 2Θ window for closer analysis. The lower panel indicates the phase

assignment to the respective reference structures of NiO (PDF #047-1049), Gd₂O₃ (PDF #012-0797) and metallic Ni (PDF #004-0850).

Table 1: Summary of structural parameters extracted from powder XRD patterns by Rietveld refinement of NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO nanofibers.

Sample	NiO phase				Gd ₂ O ₃		Ni metal	
	Lattice parameter (Å)	Weight fraction (%)	Crys. size (nm)	Microstrain x 10 ⁻⁴	Weight fraction (%)	Crys. size (nm)	Weight fraction (%)	Crys. size (nm)
NiO	4.1762(2)	100	27.3(8)	1.63	-	-	-	-
Gd ₂ O ₃ /NiO	4.1767(2)	98.6(6)	18.7(5)	1.56	1.4(4)	2.9(1)	-	-
Ni/Gd ₂ O ₃ /NiO	4.1760(1)	94.4(6)	22.4(7)	1.12	3.3(2)	4.2(1)	2.3(3)	26.6(8)

The differences between the morphology of the three prepared fibers are illustrated by the scanning electron microscopy images presented in Fig. 2(a-c). The NiO fibers are large (a few hundred nanometers width) and randomly distributed with a web-like morphology, and they are constituted of NiO individual particles. This could be explained by the bending instabilities and the partial evaporation of solvents, which were linked through hydrogen bonding [64-66]. The Gd₂O₃/NiO and Ni/Gd₂O₃/NiO samples exhibit thinner (less than 100 nanometers) and longer fibers than NiO sample due to the doping with Gd. The contrast is highly regular inside the fibers for Gd₂O₃/NiO, whereas particles like globules appear in addition for Ni/Gd₂O₃/NiO. These observations are confirmed by the HRTEM investigations. NiO NFs are mainly composed of large spherical and quasi-spherical nanoparticles (Fig. S2). These NiO nanoparticles are highly crystalline in nature as revealed by the well-resolved lattice fringes of HRTEM image and the fast Fourier transform (FFT) pattern (Fig. S3 (a)). Average fringe distances of 2.05±0.05 and 2.36±0.05 Å corresponding to the (200) and (111) planes distances in NiO phase, respectively, are observed in the HRTEM image of Gd₂O₃/NiO sample (Fig. 2d). The FFT pattern Gd₂O₃/NiO sample (Fig. S3b) reveals the lattice spacings related to the (111), (200) and (220) planes of NiO as well as the (220) and (331) planes (*d* spacings of 0.19 nm and 0.12 nm, respectively) of Gd₂O₃. These results are in good agreement with XRD results, which reveals the presence of crystalline NiO and Gd₂O₃ in

Gd₂O₃/NiO sample. Moreover, EDX elemental mapping shows that the Gd, O, and Ni elements were uniformly distributed in Gd₂O₃/NiO nanofibers (Fig. 2e-h), confirming the incorporation of Gd into the NiO lattice. In contrast, Gd was mostly observed on the surface of NiO fibers in Ni/Gd₂O₃/NiO sample ((Fig. 2j-m)), which can be explained by the segregation of Gd₂O₃ and metallic Ni phases after calcination in Ar atmosphere as coaxial nanofibers structure. The FFT pattern of Ni/Gd₂O₃/NiO (Fig. S3-c) confirms the formation of the cubic Ni metal ((111) plane correspond to *d* distance of 0.2 nm) in addition to NiO and Gd₂O₃ phases. Moreover, FFT analysis shows that the spherical nanoparticles observed on the surface of the NiO fibers (Fig. 2c) are mainly metallic Ni. These results are in good agreement with those obtained from Rietveld refinement of XRD data (see Table 1). Moreover, AAS analysis demonstrated that Ni:Gd atomic ratio is about 2.008:0.053 in both Gd₂O₃/NiO and Ni/Gd₂O₃/NiO samples. The lower amount of Gd in the samples if compared with that used in the electrospinning experiments (i.e., Ni:Gd mole ratio = 2.009:0.106) suggests that not all Gd precursor has been successfully loaded on the NiO nanofibers. However, the similar content of Ni and Gd in both Gd₂O₃/NiO and Ni/Gd₂O₃/NiO nanofibers indicates that the two samples differ only in the structure and morphology.

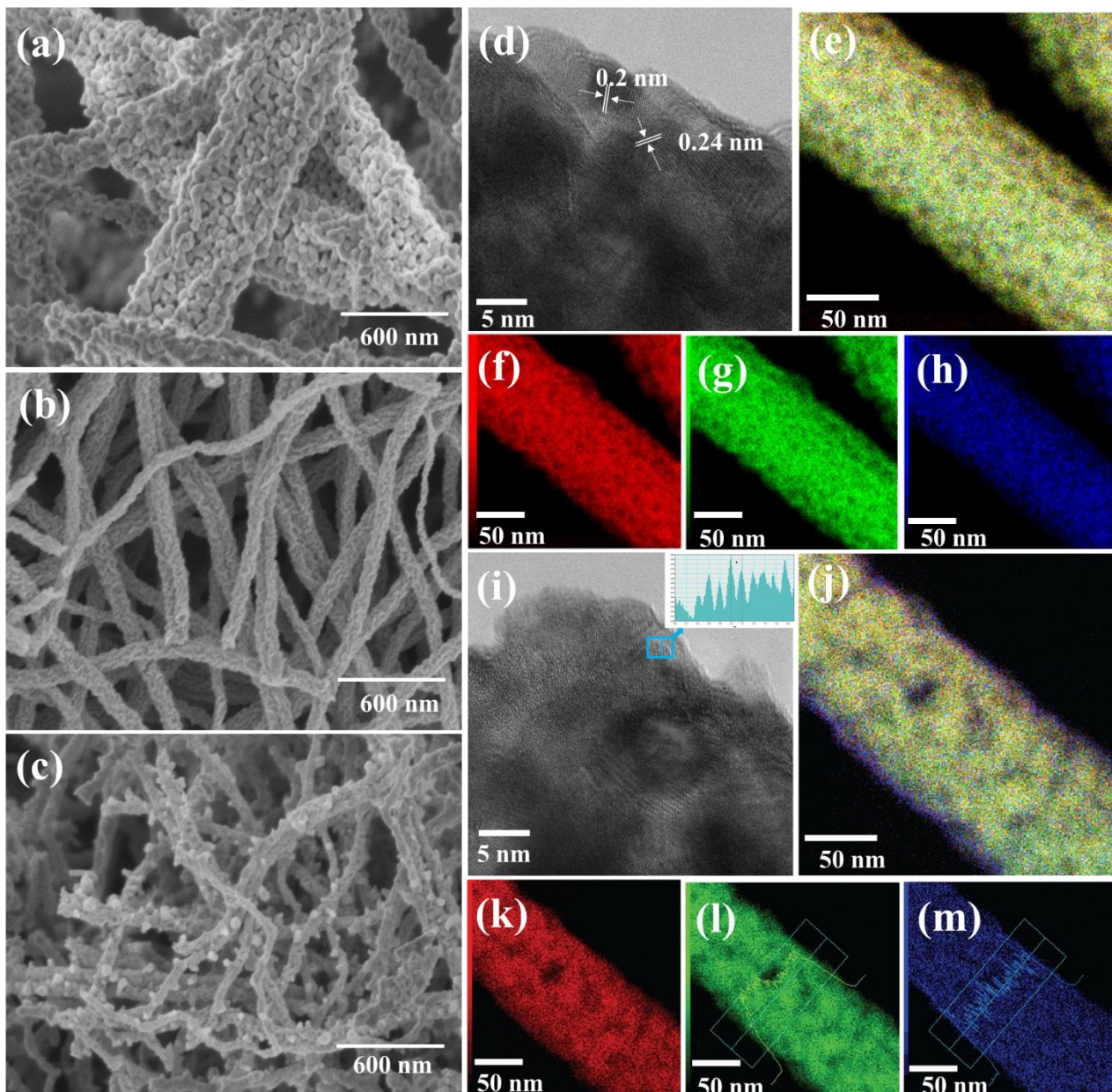


Fig. 2: Field emission SEM images of the prepared nanofibers; NiO (a), Gd₂O₃/NiO (b), and Ni/Gd₂O₃/NiO (c). High-resolution transition microscope (d and i) with EDX elemental mapping (e-h and j-m) of Gd₂O₃/NiO (d, e-h) and Ni/Gd₂O₃/NiO (i, j-m) and the fast Fourier transform (FFT) pattern of the area marked by the blue square box of Ni/Gd₂O₃/NiO and the corresponding intensity profiles in the inset (i), the oxygen (f and k), nickel (g and l) and gadolinium (h and m). The line-scans in (l) and (m) images confirm the segregation of gadolinium on the surface of nanofibers.

XPS measurements further revealed the elemental compositions, chemical bonding, and oxidation states of Ni, O, and Gd. As shown in Fig. S4, the survey XPS spectra of prepared NFs confirm the elemental composition of the obtained fibers and the presence of a small amount of carbon originated from organic acetate or PVP materials used in the synthesis. The high-resolution Ni 2p, Gd 4d and O 1s spectra are shown in Fig 3a-c. The Ni 2p_{3/2} spectra (Fig. 3a) of NiO and Gd₂O₃/NiO nanofibers can be fitted with two peaks at 853.9 and 855.5 eV with a broad satellite peak at around 861.1 eV, in good agreement with the previous reports for NiO [67]. For Ni/Gd₂O₃/NiO, these XPS peaks are shifted to lower binding energy, suggesting a decrease of the oxidation state of nickel cations, in agreement with the observation of Ni metal by XRD (Fig. 1). The O 1s spectra (Fig. 3b) can be deconvoluted into three peaks around 529, 531 and 532 eV corresponding to the oxygen lattice O²⁻, hydroxides and adsorbed oxygen (i.e. adsorbed H₂O), respectively [50]. For the Ni/Gd₂O₃/NiO sample, the peak corresponding to the lattice oxygen is shifted to lower binding energy, which can be explained by a decrease of the oxygen content in this sample in connection with the reducing conditions of the annealing. Moreover, a high amount of hydroxides is observed on the surface of Ni/Gd₂O₃/NiO sample calcined in Ar. The Gd 3d spectra of Gd₂O₃/NiO and Ni/Gd₂O₃/NiO (Fig 3c) can be fitted with one peak located at 1189 eV assigned to Gd 3d_{5/2} of Gd₂O₃ [68].

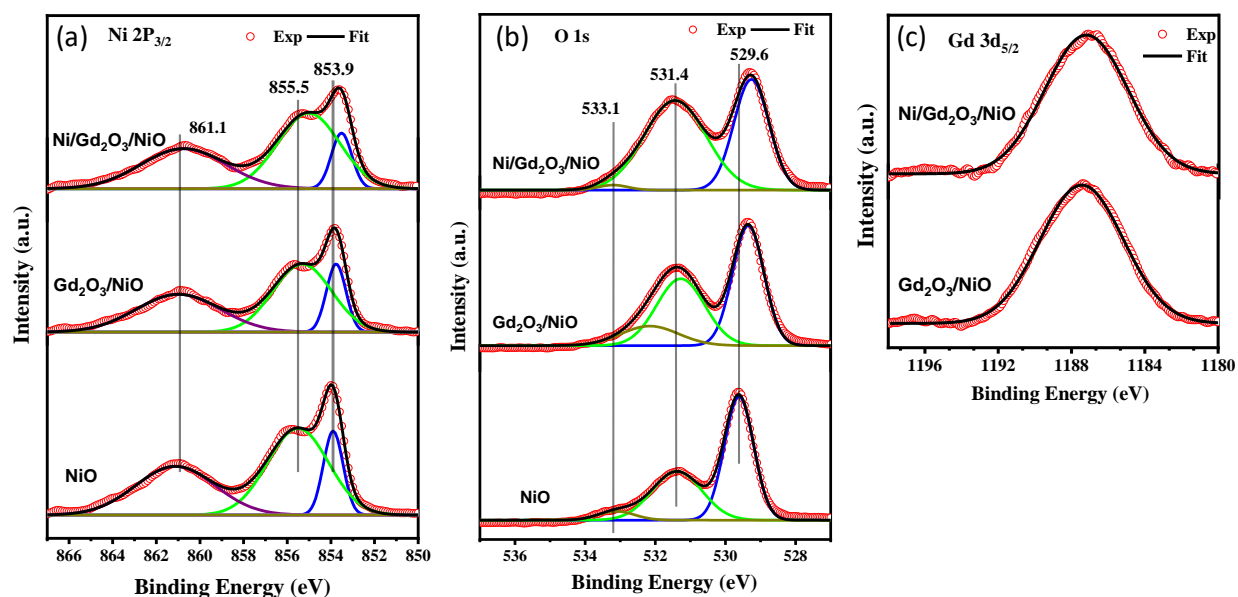


Fig. 3: High-resolution XPS spectra of Ni 2p (a), O 1s (b), and Gd 3d (c) for NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO nanofibers.

Fig. 4 shows the room temperature continuous-wave (cw) EPR spectra of NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO samples. The spectra were normalized to sample mass. For all samples, the EPR spectra show a broad line around $g \approx 2.3$ with the intensity and ΔB_{pp} linewidth varying in a complex way for the different samples. The observed g -values are within the range of g -values previously reported for NiO particles [69, 70]. For the Gd₂O₃/NiO sample, a clear decrease in EPR intensity can be detected compared to NiO sample, supporting the assumption that mainly Ni species contribute to the detected signal. The intensity decrease is qualitatively comparable to previous results on Gd-doped NiFe₂O₄, as reported by Dixit *et al.* [71]. It is perceivable that Gd³⁺ ions replace Ni-ions lowering, thereby the signal intensity attributed to Ni-ions. The EPR spectra with a dominant broad signal centered around $g \approx 2.3$ did not allow for a clear identification of Gd³⁺ related signals expected at g -values ≤ 2.05 [72]. The ΔB_{pp} linewidth is slightly higher for Gd₂O₃/NiO compared to NiO despite the decrease in intensity indicative for significant g -value broadening evidenced for both samples in 34 GHz measurements (data not shown). The Ni/Gd₂O₃/NiO sample exhibits the highest EPR intensity and ΔB_{pp} linewidth suggesting the highest number of EPR-active species within the sample series. There are several possible origins for this intensity enhancement: Compared to Gd₂O₃/NiO, the number of replaced Ni ions is expected to be decreased, as increased Gd₂O₃ segregation is evidenced by XRD. Additionally, the fibers size and defect density may affect the signal, as EPR detects only a part of the Ni species in NiO exhibiting in bulk antiferromagnetic ordering ($T_{N\acute{e}el} = 250$ °C) [70, 73]. Moreover, as segregation of Ni metal is revealed by XRD analysis, metallic Ni nanoparticles ($g \approx 2.25$ depending on the distance between particles) [74-76] may contribute to the observed signal.

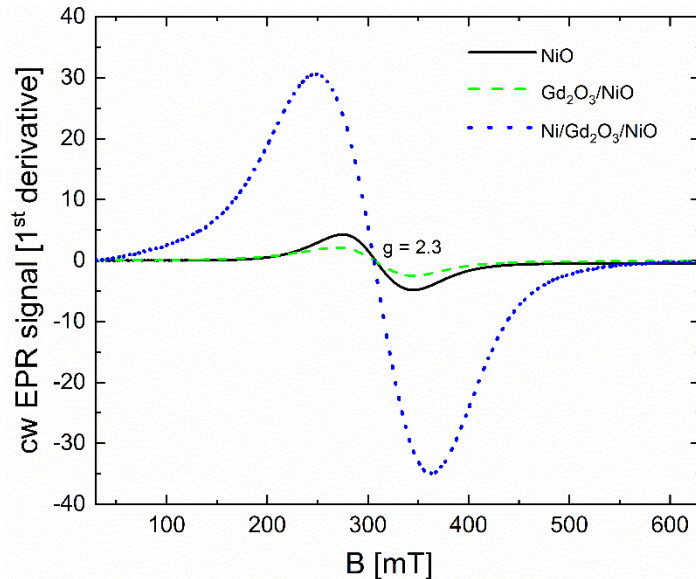


Fig. 4: Room temperature cw EPR spectra of NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO nanofibers (9.78 GHz, 5 G, 100 kHz, 2 mW mw power). Spectra are normalized to sample mass.

The mechanism of formation of Ni/Gd₂O₃/NiO heterostructure during calcination in argon atmosphere can be explained as follows. During calcining the electrospun nanofibers in air or oxygen atmosphere, many oxygen vacancies are usually expected to be generated in the NiO lattice, while on cooling, the atmospheric oxygens fill these oxygen vacancies in the NiO nanofibers again. In contrast, during calcining the nanofibers in oxygen-free atmosphere (e.g. argon), there are no sufficient oxygens to fill back the generated oxygen vacancies on the surface of the nanofibers. In consequence, Gd₂O₃ is segregated to the surface as well as a partial reduction of NiO into metallic Ni is taken place as the charge compensation. Therefore, the Ni/Gd₂O₃/NiO heterostructure is formed only while performing the calcination of the nanofibers in argon atmosphere. Our finding is consistent with previous works showed the formation of similar Ni/NiO heterostructure by calcining electrospun Ni-organic nanofibers in argon atmosphere [49].

The electrocatalytic activities of NiO, Gd₂O₃/NiO and Ni/Gd₂O₃/NiO for HER were investigated, and commercial Pt tested for comparison (Fig 5). The LSV curve in Fig.5a revealed that the NiO sample shows poor performance for HER. In contrast, Gd₂O₃/NiO exhibits good HER activity due to the substitution of Ni²⁺ with Gd³⁺ in the NiO lattice as confirmed in the previous section on the sample characterization. The presence of Gd₂O₃ as impurity could be another reason for the good

electrocatalytic activity of this sample, since such an enhancement of the electrocatalytic activity is achieved by adding Gd/Gd₂O₃ particles in Ni-Co and Ni-CeO₂-Gd electrodes to HER [51, 52]. The highest HER activity is observed for Ni/Gd₂O₃/NiO, requiring only a small overpotential of 190 mV to achieve a current density of 10 mA/ cm². However, the activity is as still slightly lower than that of a Pt plate (160 mV@10 mA/ cm²), whereas the onset potential of Ni/Gd₂O₃/NiO is lower than that of Pt, which recommended it for potential industrial application in HER. The high activity of Ni/Gd₂O₃/NiO sample can be explained by four reasons: (i) the segregation of Gd₂O₃ on the surface of NiO fibers, (ii) formation of active Ni metal via the reduction in Ar atmosphere, (iii) the smaller fiber diameter and (iv) high amount of OH⁻ on the surface of the fibers.

Tafel slopes are given by fitting the linear regions of Tafel plots to the Tafel equation ($\eta = b \log |j| + a$, where b is the Tafel slope and j the current density). As demonstrated in Fig. 5c, the Tafel slope value of Ni/Gd₂O₃/NiO nanofibers (45 mV/dec) is smaller than those of NiO (120 mV/dec), and Gd₂O₃/NiO (53 mV/dec) but larger than that of Pt (30 mV/dec). The current exchange densities (j_0) of prepared samples are estimated from the Tafel plots via extrapolation. The values of j_0 for NiO, Gd₂O₃/NiO and Ni/Gd₂O₃/NiO nanofibers were gathered in Table 2, confirming the superior performance of Ni/Gd₂O₃/NiO. Ni⁰ has a convenient H atom binding energy close to Pt [77, 78]. Whither, Ni⁰ on the surface of Ni/Gd₂O₃/NiO nanofibers would facilitate H adsorption and thus the Volmer process. The roles of segregated Gd₂O₃ on the surface of Ni/Gd₂O₃/NiO could accelerate both Volmer and Heyrovsky processes and reduce the resistance to drive HER with higher exchange current density at low overpotentials via liberations of additional reactive sites. Wheresoever, the OH⁻ generated by H₂O splitting could preferentially attach to a Gd₂O₃ site at the interface due to strong electrostatic affinity to the locally positively charged Gd³⁺ species and more unfilled 5d orbitals. Furthermore, the segregation of Gd₂O₃ to Ni-based materials could increase their corrosion resistance and stability [54]. Additionally, the voltammetric study of NFs within the potential range of +0.1 to +0.3 V, where no faradic reaction occurred (Fig. S5), is used to calculate the double-layer capacitance (C_{dl}) of NFs as illustrated in Fig. 5d and summarized in Table 2. The C_{dl} is linearly proportional to the effective electrochemical active surface area (EEASA). Electrochemically active surface area (ECSA) was evaluated from the following equation; $ECSA = C_{dl}/C_s$, where C_{dl} is the electrochemical double-layer capacitance and $C_s = 40 \mu\text{F}/\text{cm}^2$, is the capacitance of an atomically smooth planar surface [79]. Ni/Gd₂O₃/NiO catalyst has a C_{dl} value 1.2 and 6.6 times higher than Gd₂O₃/NiO and NiO, respectively. The tests mark

that more active sites are available for Ni/Gd₂O₃/NiO catalysts. Long-term durability for HER is of great significance for industrial applications. The chronoamperometric response for 60h (Fig. 5e) shows a slight current attenuation of 5% after 60h of continuous testing [80]. Likewise, the working electrode was submitted to 5000 cycles of a continuous cyclic voltammetry measurement between 0 and -0.3V (vs. RHE). As demonstrated in Fig. 5f, the LSV curves before and after 5000 CV test closely overlap, especially in the low overpotential region. The SEM image of the prepared Ni/Gd₂O₃/NiO nanofibers after the 60h electrolysis test in Fig. S6 was revealed that the morphology remains unaltered. We can also note that the crystallinity of Ni/Gd₂O₃/NiO nanofibers (Fig. S7) was stable after 60h as confirmed by XRD. These results confirm that the Ni/Gd₂O₃/NiO catalyst possesses superior stability in the long term HER process compared to the previously reported NiO system (Table S1) [3, 48-53, 81].

Moreover, the faradic efficiency of Ni/Gd₂O₃/NiO of about 98 % was determined by GC measurements of evolved H₂, as shown in Fig. 5g. In addition, the highest faradic efficiency could be attributed to the enrichment of electron transfer in Ni/Gd₂O₃/NiO as seen from EIS measurements of Fig. 5h. To determine the internal resistance and charge transport of the prepared nanofibers, electrochemical impedance spectroscopy measurements were performed. Fig. 5h shows the Nyquist plot of the prepared NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO nanofibers in the frequency range of 100 kHz to 0.1 Hz with a signal amplitude of 10 mV. The EIS plot can be easily distinguished into a small semicircle at the high-frequency region, which identified with Randles cell and a straight line with a slope towards the low-frequency region where semi-infinite diffusion is the rate-determining step with Warburg impedance. The semicircle represents the charge transfer process, and the sloped line represents the capacitance of the double layer of the nanofibers with Warburg impedance. The equivalent series resistance (ESR) could be estimated from the intercept at the real impedance axis; it was found to be around 0.6 Ω , which constitutes the electrolyte resistance, the resistance at electrode-electrolyte interface and the electrode material internal resistance. The semicircle diameter value reveals the charge transfer resistance (R_{ct}), as illustrated in Table 2. The impedance spectrum was subjected to the Randles equivalent circuit with mixed kinetic and charge transfer control, as shown in the inset of Fig. 5h, which consists of bulk solution resistance (R_s), charge transfer resistance (R_{ct}), Warburg impedance related to the electrolyte ion diffusion (Z_w) and double-layer capacitance (C_{dl}). The lower value of R_{ct} was attributed to the high interfacial conductivity of Ni nanoparticles on the surface of NFs of Ni/Gd₂O₃/NiO and its

large slope in the low-frequency region of the Nyquist plot was ascribed to the Warburg behaviour, which arises from the fast ion diffusion across the electrode-electrolyte interface.

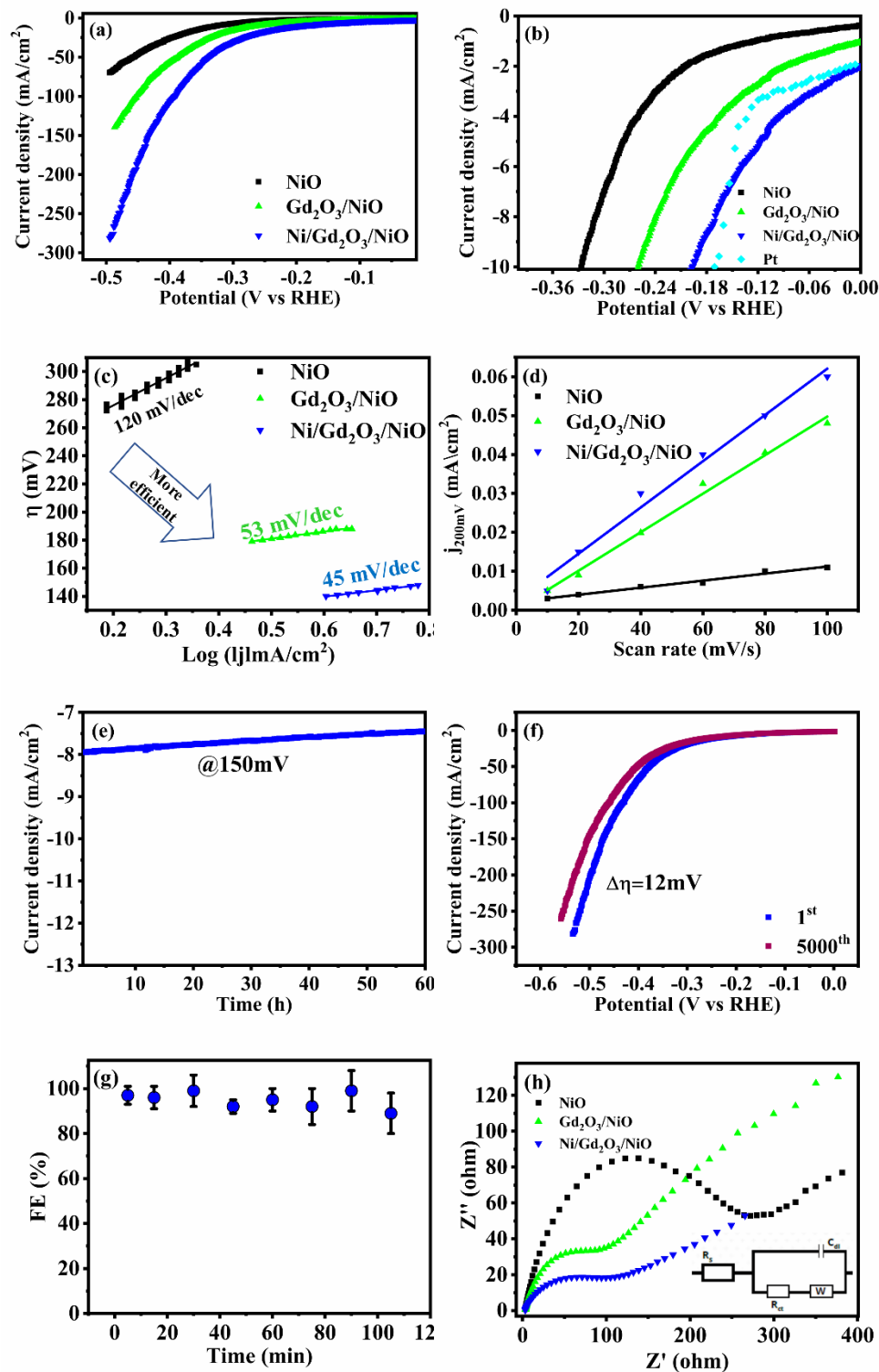


Fig. 5: a) LSV curves of NiO, Gd₂O₃/NiO and Ni/Gd₂O₃/NiO NFs for HER at 5mV/s in 1M KOH, b) LSV curves at 10 mA/cm² of the NFs and commercial Pt at 5mV/s in 1M KOH, c) Tafel plots of prepared NFs, d) estimation of C_{dl} through plotting the current density variation ($\Delta j = (j_a - j_c)/2$), at 200 mV vs. RHE; data obtained from the CV in Fig.S2) against scan rate to fit a linear regression, e) chronoamperometry test of Ni/Gd₂O₃/NiO at 150 mV, f) LV curves before and after 5000CV test of Ni/Gd₂O₃/NiO electrode at 5mV/s in 1M KOH, g) Faradic Efficiency of Ni/Gd₂O₃/NiO at 350 mV vs. RHE for HER in 1M KOH saturated with Ar for 30 min before the experiment, the concentration of evolved H₂ was quantified every 15 min and h) EIS Nyquist plots in a frequency range of 0.1Hz to 1MHz of NFs with equivalent circuit proposed in the inset.

HER reaction mechanism

The Tafel slope was revealed the mechanism and kinetics of the HER reaction. HER mechanism in alkaline media follows either the Volmer – Heyrovsky or Volmer – Tafel reaction. A Tafel slope (b) of 120, 40 or 30 mV/dec should be obtained when the Volmer, Heyrovsky or Tafel reaction is rate-determining step (RDS), respectively.

- Volmer reaction is electroreduction of water molecules with electrons on the active sites of the cathode ($* + \text{H}_2\text{O} + \text{e}^- \rightarrow * \text{H}_{\text{ads}} + \text{OH}^-$),
- Heyrovsky reaction is electrochemical hydrogen desorption ($* \text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 \uparrow + \text{OH}^-$),
- Tafel reaction is chemical desorption ($2\text{H}_{\text{ads}} \leftrightarrow \text{H}_2 \uparrow$).

As illustrated in Fig. 6, the HER at Ni/Gd₂O₃/NiO NFs surface with b = 45 mV/dec follows a Volmer-Heyrovsky mechanism, and the RDS is determined by electrochemical desorption (H₂O discharge and desorption of H₂ from the catalyst surface).

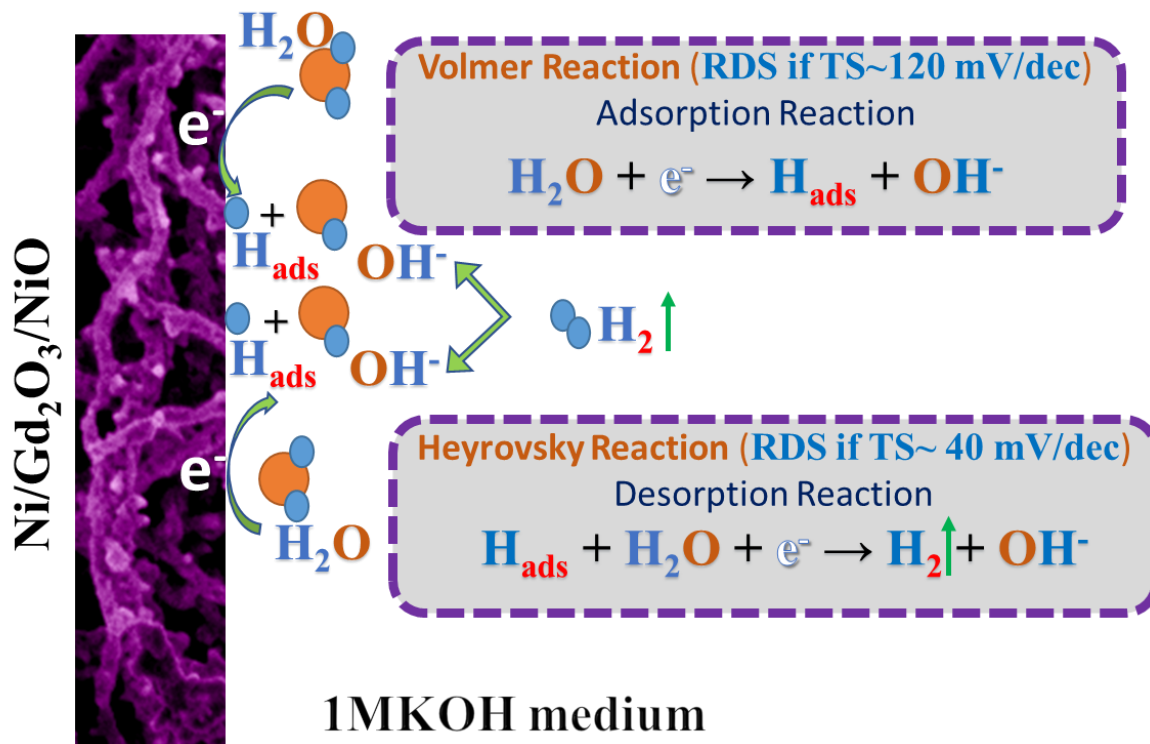


Fig. 6: Mechanism of HER on the surface of Ni/Gd₂O₃/NiO NFs.

Table 2: A summary of the electrochemical data of NiO, Gd₂O₃/NiO, and Ni/Gd₂O₃/NiO nanofibers for HER.

NFs	η_{10} (mV)	η_{onset} (mV)	TS_{HER} (mV/dec)	Cdl ($\mu\text{F}/\text{cm}^2$)	ECSA (cm^2)	j_0 (mA/cm^2)	R_s (Ω)	R_{ct} (Ω)
NiO	326	233	120	90	2.24	1.21	3.2	349
Gd ₂ O ₃ /NiO	230	139	53	495	12.37	1.64	3.5	114
Ni/Gd ₂ O ₃ /NiO	190	89	45	594	14.85	1.85	3.1	93

η_{10} : Overpotential at 10 mA/cm², η_{onset} : Onset potential, TS: Tafel slope of HER,

Conclusion

Simple and cost-effective NiO, Gd₂O₃/NiO and Ni/Gd₂O₃/NiO nanofibers prepared by electrospinning have been designed as superior HER electrocatalysts. In short, Ni/Gd₂O₃/NiO has the lowest one set potential ~ 32 mV, the smallest Tafel slope value 45 mV/dec and the highest exchange current density of 1.85 mA/cm², i.e; characteristics comparable to most noble metal-free catalysis. This specific new catalyst design is promising for key renewable energy systems. Based

on experimental studies, we demonstrated that the chemical and electrical properties of NiO NFs are successfully optimized through Ni/Gd₂O₃/NiO heterostructures; the Gd ions doped on NiO NFs and the segregation of Gd₂O₃ on the surface of NiO fibers remarkably enhance their electronic conduction and promote HER reaction kinetics simultaneously. Ni/Gd₂O₃/NiO offers the advantages of long-term durability after an accelerated scan of 5000 cycles as well as ready integration into an electrolyzes for HER, affording better performance than benchmark Pt catalysts.

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