Double layer lanthanide –Pt/TiO₂ nanotube arrays electrode as a cost-highly efficient electrocatalyst for hydrogen evolution in acid media

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ABSTRACT
Self-organized anodic double layer TiO₂ nanotube arrays (TNTAs) were sensitized by an electrochemical anodization process on a Ti sheet with a two-step anodization method. The prepared sample, followed by hydrothermal treatment with Nd(NO₃)₃ and/or Gd(NO₃)₃ and/or PtCl₄ solution at 180 °C for 2 h, produced Nd-Pt-TNTAs, Gd-Pt-TNTAs, Nd-Gd-Pt-TNTAs and Pt-TNTAs. The morphological and structural properties were studied by SEM, XRD and Raman spectra techniques. The hydrogen evolution reaction (HER) performance on Lanthanides-Pt-TNTAs was investigated using the Tafel linear polarization technique. The calculated values of the activation energy are in good agreement with the trend in catalytic activity. The excellent performance of doped TNTAs with low activation energy (Eₐ) is due to the formation of an excitation energy level below the conduction band of TiO₂ from the binding of electrons with oxygen vacancies decreasing the excitation energy resulting in robust electrocatalytic activity. The very low value of Eₐ for Nd-Gd-Pt-TNTAs (2.02 kJ/mol) compared to other electrochemical catalysts used for hydrogen evolution reactions containing titanium nanotubes was achieved for the first time. This makes the Lanthanides –Pt-TNTAs prepared in the present work optimal catalysts for electrodes and promising for applications in fuel cells or as water splitting materials.

HIGHLIGHTS
- Synthesis of self-organized anodic double layer TiO₂ nanotube arrays (TNTAs) on a Ti sheet with a two-step anodization method.
- Nd, Gd, Pt were deposited on anodic TNTAs arrays by hydrothermal method.
- The HER mechanisms on Lanthanides-Pt-TNTAs in acidic media has been discussed.
- The order of catalytic activity based on the values of activation energy was Nd-Gd-Pt-TNTAs > Gd-Pt-TNTAs > Nd-Pt-TNTAs > Pt-TNTAs > undoped TNTAs.

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1. Introduction

Recently, hydrogen has been recognized as a renewable, clean, high energy density fuel alternative to traditional fossil fuels for future energy applications. This is even more important with increasing global energy and environmental concerns caused by the over-consumption of traditional fuels [1–3]. Of all the developed technologies, water splitting by either electrolysis or photoelectrolysis represents the most effective and environmentally friendly approach to sustainably produce high purity Hydrogen [4–6]. The hydrogen evolution reaction (HER) mechanism begins by the adsorption of H on the catalyst surface [7]. Special properties play an important role in selecting catalytically active materials for hydrogen evolution, such as: (a) excellent thermodynamics and kinetics for hydrogen evolution (low overpotential for HER), (b) a large active surface area per unit volume ratio, (c) long durability and (d) low cost [7–11]. The HER mechanism includes hydrogen atom generation (Volmer step), which often uses noble metals such as Pt or Pd [3,12] and hydrogen recombination (Tafel or Heyrovsky step), which has been stimulated by some active metals or compounds [9,10,13]. Furthermore, bifunctional catalysts which stimulate both the charge transfer and chemical or electrochemical recombination processes are of interest.

TiO₂ nanotubes arrays (TNTAs) are one of the few high-quality nanotubular materials. They can be used as energy storage materials or for energy production [14]. The application of TiO₂ nanotubes is possible due to their high specific surface area, high chemical stability and catalytic activity and excellent performance in alkali and acidic environments. Su et al. [15] revealed that N-doped TiO₂, SrTiO₃ and TiO₂ nanotubes facilitated the migration of photogenerated electrons from the bulk to the surface of the multi-junction photocatalysts. This is resulting in retarded charge recombination rates and increased H₂ evolution rates. Reddy et al. [16] used Cu/Ag quantum dots on TiO₂ nanotubes as highly efficient photocatalysts for enhanced solar hydrogen evolution. In general, the positive effects of metal deposition on TiO₂ surfaces results in the suppression of electron-hole pairs on the surface of the catalyst and an excellent mobility of charge carriers and high absorption cross-sections [3,6]. Additionally, the hydrogen adsorption before the HER has a central role in modern electrochemistry [7]. According to the volcano curve for HERs, the strength of the metal-hydrogen bond for Pt is very close to zero [17], and therefore, Pt should provide a good catalytic effect on the recombination of hydrogen atoms.

Therefore, in this study, a group of advanced catalysts for electrochemical hydrogen evolution reaction (HER) have been developed which have bifunctional electrocatalysts with activity in acidic media. These catalysts are Lanthanide/Pt/TiO₂ nanotubes arrays (TNTAs). To the best of our knowledge, this is the first systematic report on the application of Lanthanide/Pt/TNTAs composites for HER electrocatalysis. The possible electrolysis mechanism and enhanced HER with Lanthanide/Pt doped are discussed in detail.

2. Experimental

2.1. Electrochemical synthesis of self-organized TNTAs

The anodization of titanium metal to generate nanostructured TiO₂ has been achieved using the experimental rig described schematically in Figure 1(a). The system developed includes an electrochemical cell, a power supply capable of operation as a voltage source (Germany, PeakTech, 6005D)/current measuring device (US & Canada, Agilent digit multimeter, 34450A). The cell was designed to be made in a 100 mL Teflon beaker. At the anode, a titanium sheet (Alfa Aesar, purity 99.5%) having an area of approximately 1 cm²
was left exposed to the electrolyte. Platinum wire (Alfa Aesar, purity 99.95%) was used as a cathode. Figure 2 shows the anodization synthesizing of undoped TNTAs in a non-aqueous solution containing small amount of a fluoride salt. In the first-step anodization, TNTAs were prepared at applied voltage of 60 V for 1 h. After ultrasonic removal of the of performed TNTAs layer, the nano concaves Ti substrate was the second-step anodizing at 60 V for 1 h. Nd-Pt-TNTAs, Gd-Pt-TNTAs, Nd-Gd-Pt-TNTAs and Pt-TNTAs were prepared by the hydrothermal method. The as prepared anodized TNTAs were immersed into 30 mL different doped solution, 10:1 of Nd(NO$_3$)$_3$:PtCl$_4$, Gd(NO$_3$)$_3$:PtCl$_4$, [Gd(NO$_3$)$_3$+ Nd(NO$_3$)$_3$]:PtCl$_4$, (Sigma Aldrich, purity 99.9%), in a Teflon-lined stainless steel autoclave and kept at 180 °C for 2 h as shown in Figure 1(b). After cooling to the room temperature, the sample was removed from autoclave, rinsed with deionized water and finally dried in air.
Figure 2. Schematic diagram of the TNTAs preparation by electrochemical synthesis.
2.2. Characterization of electrocatalysts

The morphologies and composition of the undoped and doped TNTAs samples were examined by scanning electron microscopy and Energy Dispersive X-ray analysis, respectively (SEM, EDX, Superscan SS-550, Shimadzu, Japan). The crystal structure of the as prepared samples was performed by X-ray diffraction (XRD, Shimadzu, XRD-7000, Japan) at 40 kV and 30 mA, using CuKα incident beam (λ = 0.154 nm). Raman spectroscopy was performed on a Raman microscope (Raman, Sentrarra, Bruker, USA) coupled to a Leica microscope (optical microscope, Olympus BX series, USA) to produce 532 nm excitation radiation.

2.3. Hydrogen production activity

Direct current (DC) polarization measurements of hydrogen evolution in 0.1 M H2SO4 were carried out using a conventional three-electrode cell. The cell was composed of synthesized undoped and doped TNTAs used as working electrode (WE) with working area of 1 cm², a platinum wire counter electrode (CE) and a saturated calomel electrode (SCE) as a reference electrode (RE). The linear polarization measurement was made starting from −0.5 V to −0.7 V, at a scan rate of 1 mVs⁻¹. The activation energy of the HER on Lanthanide-Pt-TNTAs catalysts was also measured from 303 K to 338 K.

The interfacial properties between the electrochemical anodization synthesis TNTAs, Nd-Gd-Pt-TNTAs/0.1 M H2SO4 interface was investigated using Electrochemical Impedance Spectroscopy (EIS) measurements carried out with a sinusoidal voltage of 10 mV per decade. The frequency range was from 100 kHz to 0.1 Hz, at a potential of −0.5 V vs. reference electrode.

3. Results and discussion

3.1. Morphological and crystalline phase characterization

The surface structure properties play a key role in electrocatalytic performance [18]. Some research efforts to further increase the surface area of anodic TiO2 nanotubes have been found, such as fabrication of multilayer TiO2 nanotube arrays with extra porous interlayers [19–21]. The TiO2 tubular structure evolves from single layer to a double-layer structure of nanotubes under two-step anodization at high voltage. A possible method to grow high-aspect-ratio double-layer TNTAs employs the top layer grown as a protective layer to facilitate bottom layer growth [20].

Figure 3(a,a’) shows SEM images of TiO2 nanotube arrays fabricated under one-step anodization after calcination treatment at 450 °C for 3 h. The direct anodization at 60 V for 1 h leads to the formation of single layer TiO2 nanotube arrays. There are no intact nanotubes, just some small holes. These tubes have poor growth and smooth walls with an average length of approximately 4.908 μm, and the top surface image shows that the inner diameter is approximately 75.542 nm with a merge wall of thickness approximately 109–120 nm. The cross-sectional view of two-step anodization TNTAs after calcination treatment at 450 °C for 3 h depicts that the upper layer reaches a thickness of approximately 7.44 μm, (Figure 3(b,b’)), where the lower layer is 6.35 μm thick and the tube diameter becomes slightly larger (~86.4 nm).

For modified TiO2 nanotube arrays, Figure 4(a,a’) for Nd-Pt-TNTAs, (b,b’) for Gd-Pt-TNTAs, (c,c’) for Nd-Gd-Pt-TNTAs and (d,d’) for Pt-TNTAs show top-view and cross-sectional views, respectively, after calcination treatment at 450 °C for 3 h. All nanotube
Figure 3. SEM images of (a, b) top surface; (a', b') cross-sectional view; (a'', b'') EDX of one step anodization and two steps TNTAs, respectively.
Figure 4. SEM images of (a, b, c, d) top surface; (a', b', c', d') cross-sectional view; (a'', b'', c'', d'') EDX of Nd-Pt-TNTAs; Gd-Pt-TNTAs; Nd-Gd-Pt-TNTAs; Pt-TNTAs, respectively.
Figure 4. Continued
arrays show uniform, highly ordered and vertically oriented morphologies over all of the observed area. In addition, no oxide ripples were observed on the outer walls of the doped TNTAs. This confirms that in situ doping impedes the metal ions inside the TiO₂ lattice. The incorporation of rare element metals (REM) in the TiO₂ lattice would enhance the conductivity of titanium. Additionally, in relation to REM nanoparticles, Pt nanoparticles are more effective for hydrogen production. The average diameters of Nd-Pt-TNTAs, Gd-Pt-TNTAs, Nd-Gd-Pt-TNTAs and Pt-TNTAs are 84.67, 85.39, 102.96 and 92.89 nm, respectively, which agrees with lanthanide-doped TNTAs [22–24] and a double layer length of approximate 12.22 μm. Notably, the hydrothermal treatment and in situ modification of TNTAs with lanthanides -Pt did not influence the morphology of the REM-Pt-TNTAs; they are morphological stable. The doped ions impede the TiO₂ lattice, resulting in no change in the morphology of TNTAs after REM-Pt incorporation.

The approximate composition of undoped TNTAs at step one and step two was calculated from EDX spectrum, Figure 3(a”,b”). Peaks of Ti, O and F are clearly observed on the coating. The very low mass fraction of F reveals the remaining fluoride inside the tubular structure. The EDX pattern of Lanthanides-Pt-doped TNTAs in Figure 4(a”,b”,c”) show approximately uniform distribution of Nd and/or Gd nanoparticles with Pt. The distribution of Pt nanoparticles is much larger in TNTAs lattice, Figure 4(d”). The EDX results are shown in Table 1. Nearly 1.23% and 2.42% loading of Nd and Pt, respectively, is seen in Nd-Pt-TNTAs, 2.05% and 4.90% of Gd and Pt in Gd-Pt-TNTAs, approximately 0.60%, 0.43% and 4.41% of Nd, Gd and Pt in Nd-Gd-Pt-TNTAs and approximately 5.11% Pt loading in Pt-TNTAs. Notably, there was an absence of F pattern in the EDX results.

According to above results, in our case, when the first step was anodizing of 60 V applied for 1 h, an organized nanostructure of double-layered nanotubes array formed as explained in Figures 3(a,a’) and 5. At first, the oxide layer on the Ti sheet formed due to Ti metal oxidation according to Equations (1–3) [25].

\[ \text{Ti} \rightarrow \text{Ti}^{4+} + 4e \]  
\[ \text{Ti}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4 \text{H}^+ + 4e \]  
\[ \text{Ti}^{4+} + 2\text{O}^{2-} \rightarrow \text{TiO}_2 \]  

Simultaneously, the counter reaction which is hydrogen evolution, takes place at the cathode, Equation (4).

\[ 4\text{H}_2\text{O} + 4e \rightarrow 2\text{H}_2 + 4\text{OH}^- \]  

According to the field-assisted dissolution, this counter reaction is the formation of the nanotube structures which is mainly associated with the fluoride ions. During the hydrolysis reaction, electroneutrality is maintained due to the accumulation of H⁺ ions. F⁻ ions migrate to the H⁺ sites. When a critical concentration is reached in the local regions, the dissolution of TiO₂ occurs from the formation of aqueous hexafluorotitanate (fluoride ions form a complex with Ti⁴⁺) according to Equation (5).
Normally, the formation of TNTAs during anodization process depends on three simultaneous reactions. The first is field-assisted oxidation of Ti metal to form TiO₂, followed by field-assisted etching of the oxide layer by the electric field weakening the bond between Ti and O, and cause the chemical dissolution of TiO₂ by fluoride ions [26]. The presence of fluoride ions in the electrolyte is due to migration through the oxide film to form water soluble [TiF₆]²⁻ species, Equation (6), or due to chemical attack of the formed TiO₂, Equation (7) [27–30]. For intermediate fluoride concentrations, porous oxide or nanotube formation can be observed in this stage due to penetration of the initial compact oxide.

\[
\text{Ti}^{4+} + 2\text{H}^+ + 6\text{F}^- \rightarrow \text{H}_2\text{TiF}_6
\]  

Normalmente, la formación de TNTAs durante el proceso de anodización depende de tres reacciones simultáneas. La primera es la oxidação field-assisted de la Ti metálico para formar TiO₂, seguido de la etch field-assisted de la capa de óxido por el campo eléctrico debilitando el enlace entre Ti y O, y causando la disolución química de TiO₂ por iones fluoruro [26]. La presencia de iones fluoruro en el electrolito es debido a la migración a través de la película de óxido para formar especies solubles en agua [TiF₆]²⁻, ecuación (6), o debido al ataque químico de las formadas TiO₂, ecuación (7) [27–30]. Para concentraciones intermedias de fluoruro, la formación de óxido poroso o tubos de nanotubos puede ser observada en esta etapa debido a la penetración del óxido inicial compacto.

\[
\text{Ti}^{4+} + 6\text{F}^- \rightarrow [\text{TiF}_6]^{2-}
\]  

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O}
\]  

La formación de TNTAs en esta investigación también puede explicarse basada en el molde de burbuja de oxígeno y el modelo de corriente ionic y de electrones [31–33]. El alta
conductivity of ethylene glycol electrolyte [34], and at high voltage (about 60 V) lead to high values of both the initial electronic current (Equation (1)) at the beginning of anodization due to growth of the compact oxide layer in ethylene glycol electrolyte and ionic current chemical which contributes to the formation of the anion contaminated layer. So with the existence of the compact layer oxide and anion contaminated layer by F⁻, the electronic current is rapidly produced and accompanied with oxygen bubbles evolution. Therefore, the growth of the barrier oxide layer surrounding the oxygen bubbles in the electrolyte glycol electrolyte is rapidly forming. In addition, nanotubes are rapidly forming around oxygen bubbles [29,33,35].

Then, the as-grown nanotube layer was ultrasonically removed. In this step, the treated Ti sheets have hexagonal concave shapes in a periodic pattern, Figure 5 (stage b). These hexagonal concave shapes play a key role in the further growth of longer, well-aligned and highly organized TNTAs during the second anodizing step and inhibit random nucleation (stage c). The modification of synthesized TNTAs by hydrothermal treatment introduce the doped ions (Gd³⁺, Nd³⁺, Pt⁴⁺) at the boundary of nanostructure (stage d).

XRD was usually used to identify the crystal phase and crystallite size of TiO₂. Figure 6 shows the XRD spectrum of un-doped and doped TNTAs. The results show that all the TiO₂ nanotube arrays are highly crystalline, which mainly consist of anatase phase with peak position (1 0 1), (0 0 4) and (2 0 0) corresponding to diffraction angle (2θ) at 25.42, 38.18 and 48.10 (JCPDS No. 21-1272). The diffraction planes of anatase in Figure 6(b–d) indicate good crystallization of Nd-Pt-TNTAs, Gd-Pt-TNTAs and Nd-Gd-Pt-TNTAs and reflect a well embedded and incorporation of Nd in the TiO₂ lattice or interstitial site. The slight shift in the angel from (JCPDS, card no.: (00-029-0922) for Nd and (JCPDS, card no. (00-021-0342) for Gd, is agreement with the fact that Lanthanides have a large ionic radius than Ti⁴⁺ resulting slight defect and decreasing in crystallinity in the TiO₂ lattice when introduced [18,36]. In all doped TNTAs, a peak appears at 38.85° corresponding to (1 1 1) crystal plane of Pt(JCPDS, card no. (00-004-0802). This means that Pt is successfully dispersed in the TiO₂ lattice. The average anatase crystal size of two steps undoped and doped TNTAs was calculated using the Scherrer equation [37]. As display in Table 2, the doping does not affect the TiO₂ crystal size.
Raman spectra, as illustrated in Figure 7, clearly show that all TNTAs are present mainly as anatase in good agreement with XRD results. Raman peaks are at approximately 144 (E_g), 197 (E_g), 393 (B_1g), 514 (A_1g) and 635 (E_g) cm\(^{-1}\) [38]. This further supports the stabilization of the anatase phase after Lanthanides and Pt addition.

### 3.2. Hydrogen production performance

The cathodic polarization curves of various Lanthanides-Pt-TNTAs show a well-defined Tafel behavior in Figure 8, representing hydrogen production. The Pt-TNTAs and TNTAs samples were also tested under the same conditions for comparison. The corresponding results and are given in Table 3.

The ability of a given metal to catalyze the HER is usually measured by the cathodic exchange current density and Tafel slope [10,39]. Therefore, the hydrogen production reaction kinetics of electrocatalysts were investigated by the Tafel slope extracted from fitting to Tafel formula, Equation (8), of linear portions of Tafel plots in Figure 8.

\[ \eta_c = a - b \log j_c \]  

where \( \eta_c \) is the cathodic overpotential, \( j_c \) is the cathodic current density and \( b \) is the Tafel slope. Tafel slopes were obtained by fitting the linear regions of Tafel equation and are given in Table 3. The data shows that-modified TNTAs resulted in an increase in electrocatalytic activity toward HER due to enhancing the cathodic current. It is found that Nd-

### Table 2. Average crystalline size of two steps undoped TNTAs, Nd-Pt-TNTAs, Gd-Pt-TNTAs, Nd-Gd-Pt-TNTAs and Pt-TNTAs.

| Sample                                | Average crystalline size (nm) |
|---------------------------------------|-------------------------------|
| 2 st undoped TNTAs                    | 1.85                          |
| Nd-Pt-TNTAs (Ti: Nd + Pt = 10:1)      | 1.87                          |
| Gd-Pt-TNTAs (Ti: Gd + Pt = 10:1)      | 1.89                          |
| Nd-Gd-Pt-TNTAs (Ti: (Nd + Gd) + Pt = 10:1) | 1.81                          |
| Pt-TNTAs (Ti:Pt = 10:1)               | 1.83                          |

Figure 7. Raman spectra of undoped TNTAs (red), Nd-Pt-TNTAs (blue), Gd-Pt-TNTAs (green), Nd-Gd-Pt-TNTAs (pink), Pt-TNTAs (brown).
Gd-Pt-TNTAs exhibits a value of $\frac{1}{C_0}$ 68.870 m A/cm$^2$, 15 times higher than that of undoped TNTAs. The presence of approximately 5.11% of Pt in Pt-TNTAs sample, Table 1, reflects the good performance as an electrocatalyst of the corresponding sample in Table 3. The values of Tafel slope give a good indication of the HER mechanism. According to the general HER mechanism in acidic media, HER is a multistep process that takes place on the surface of catalyst. There are two proposed mechanisms, Volmer–Tafel and Volmer–Heyrovsky and both of them describe the reaction of hydrogen atom adsorption and desorption. In acidic media, the first step in HER is always the electrochemical H atom adsorption, Equation (9).

$$M + H^+ + e^- \rightarrow M - H_{ads} \quad \text{(Volmer reaction, } b = 120 \text{ mV/dec)} \quad (9)$$

This reaction is followed by either the electrochemical desorption of $H_{ads}$ as intermediate reaction, Equation (10).

$$M - H_{ads} + H^+ + e^- \rightarrow H_2 + M \quad \text{(Heyrovsky reaction, } b = 40 \text{ mV/dec)} \quad (10)$$

or by the chemical recombination of two $H_{ads}$ atoms, Equation (11).

$$M - H_{ads} + M - H_{ads} \rightarrow H_2 + 2M \quad \text{(Tafel reaction, } b = 30 \text{ mV/dec)} \quad (11)$$

The high Tafel slopes for the synthesized TNTAs in Table 3 reflect low fractional occupancy ($\theta_{H}$) of the surface by $H_{ads}$. This suggests that the Volmer reaction is the primary discharge step, i.e. the adsorption of hydrogen on the TNTAs catalyst controls the overall reaction rate at the catalyst [3,40–43].

Accordingly, a discharging reaction (Volmer reaction) rate will be occur under low coverage of $H_{ads}$ on the TNTAs catalyst due to the low free energy ($\Delta G_{H^+}=0$) of H atom adsorption.
adsorption on Pt. This is the reason that Pt-doped TNTAs in this work are considered as the best HER electrocatalyst [7,44]. Additionally, the TiO$_2$ materials are semiconductors having wide band gaps of 3.2 eV for anatase structure [29]. The improvement of electronic conductivity is, therefore, required to apply them to actual electrocatalyst supports. To improve its electrocatalytic ability, TiO$_2$ is doped by nonmetal and/or metals (in our study Lanthanides). When these atoms are doped into TiO$_2$, they create mid-band gap levels between the conduction band and valance band. These impurity levels resulting in a decrease in band gap energy [4,45].

To better compare the HER activity of synthesized TNTAs, one must understand that the HER does not occur at a reversible potential but requires a certain overpotential. The overpotential data at a certain HER rate (1 mA cm$^{-2}$) in Table 3 gives the amount of energy required for producing a specific amount of hydrogen. It can be concluded that the order of catalytic activity was also Nd-Gd-Pt-TNTAs $>$ Gd-Pt-TNTAs $>$ Nd-Pt-TNTAs $>$ Pt-TNTAs $>$ TNTAs. The same trend is observed when current density values were measured at a fixed overpotential of $-500$ mV.

Notably, it was found that the catalytic activity of intermetallics toward the HER is much higher than the activity of their individual components and, quite often, even higher than that of noble metals. This result agrees with the study by Łosiewic et al. [46]. The synergistic effect between Pt and lanthanides is clearly observed. The data showed that Nd-Gd-Pt-TNTAs have the highest catalytic activity for the HER among the prepared series.

3.3. Activation energy of HER

To gain insight on the superior performances of lanthanides-Pt-TNTAs toward HER, Tafel measurements were performed from 303 K to 338 K to estimate the temperature effect on HER and calculate activation energy for hydrogen production on the catalyst. As expected, a temperature rise, i.e. the enhancement of the thermal motion, will lead to an increase in cathodic discharge current density, Figure 9(a–e).

Activation energy values of HER can be estimated form Arrhenius equation Equation (12).

$$\log j_o = \frac{-E_a}{2.303RT} + \log A$$

where $j_o$ ($\mu$A/cm$^2$) is the cathodic current density, $A$ (A cm$^{-2}$) is the pre-exponential factor, $R$ (J/mol.K) is the universal gas constant, $T$ (K) is the absolute temperature and $E_a$ (J mol$^{-1}$) is the apparent activation energy. From the slope of the linear plot of $\log j_o$ and $1/T$, Figure 9(a–e), one can calculate the apparent activation energy. According the $E_a$ values in Table 3, again, the order of the electrocatalytic activity for HER was Nd-Gd-Pt-TNTAs $>$ Gd-Pt-TNTAs $>$ Nd-Pt-TNTAs $>$ Pt-TNTAs $>$ undoped TNTAs. This trend agreed well with the trend concluded from Tafel measurements.

The insertion of Nd and/or Gd may contribute greatly to the kinetics for the hydrogen evolution electrode reaction. The very low $E_a$ value for Nd-Gd-Pt-TNTAs makes it the best candidate for HER-based fuel cell devices with low platinum loadings.

3.4. Kinetic parameters of HER

To elucidate the origin of the improved kinetic performances of undoped-TNTAs and co-doped Nd-Gd-Pt-TNTA electrodes, EIS of the samples was conducted at an overpotential
of $-0.5$ V vs SCE in acid media. Both samples showed similar Nyquist plots and were fit using the equivalent circuit model in the inset of Figure 10 [47]. The first indistinct semi-circle represents the resistance of the TNTA layers ($R_f$) on the Ti sheet. The large semi-circle is attributed to the charge transfer resistance ($R_{ct}$) at the electrode/electrolyte interface during the hydrogen ion transport processes. The slope of the linear region is assigned to the Warburg impedance which indicates the hydrogen ion diffusion inside the electrode materials. The Nd-Gd-Pt-TNTA electrode displayed lower impedance (lower $R_{ct}$) than the TNTA electrode and exhibited smaller Faradic impedance as shown in the

![Graphs](image_url)

*Figure 9.* (a, b, c, d, e) Linear Tafel polarization curves of TNTAs catalysts for the HER recorded at various temperatures in 0.1 M H$_2$SO$_4$; (a’, b’, c’, d’, e’) Arrhenius plots.
Figure 9. Continued

Figure 10. Representative Nyquist plots recorded on undoped TNTAs and Nd-Gd-Pt-TNTAs, in 0.1 M H₂SO₄ at an over-potential of −0.5 V in acid media.
Nyquist plots and data in Table 4. The reduced impedance affords faster electron transfer between the Nd-Gd-Pt-Titanium nanotubes arrays and the interface. Therefore, the superior kinetics of the HER can be attributed to metal doping and the nanotubular structure.

3.5. Stability of Nd-Gd-Pt-TNTAs catalytic electrode

The performance stability of a catalyst is an important criterion for an electrocatalyst and it is crucial for its practical scale applications. The stability of the prepared Nd-Gd-Pt-TNTAs electrode catalyst was subjected to a potential of $-0.5 \text{ V}$ for 30 min in 0.1 M $\text{H}_2\text{SO}_4$. The current-time curve can be divided into two parts. In the first part, from zero time to 250 s, the current increased sharply as depicted in Figure 11. In the second part, the current value is constant (about $-0.001 \text{ A}$). In the time interval starting from 250 to 1800 s. This observation led us to conclude that the surface of the catalyst used in the HER is stable and does not indicate any sign of surface poisoning.

4. Conclusions

In summary, a simple electrochemical method has been used for the preparation of undoped-TNTAs with anatase phases. Doped TNTAs were prepared by the hydrothermal method. Nanoparticles Nd and/or Gd and/or Pt were doped into a TiO$_2$ lattice, which made TNTAs responsive to electrolysis. The prepared samples can achieve water-splitting electrocatalysis in
0.1 M H₂SO₄. The optimal electrode catalyst was Nd-Gd-Pt-TNTAs with a small loading of (4.41%) Pt. This catalyst had better activity (cathodic current about −68.870 μA/cm²) than undoped-TNTAs and (5.11%) Pt-TNTAs. EIS data also showed the higher catalytic performance of Nd-Gd-Pt-TNTAs compared to undoped TNTAs in HER. This result can be explained on the basis that codoped metal on TNTAs augmented the HER catalysis. The order of catalytic activity based on the values of activation energy was Nd-Gd-Pt-TNTAs > Gd-Pt-TNTAs > Nd-Pt-TNTAs > Pt-TNTAs > undoped TNTAs. This study may shed light on the improvement of the water-splitting electrocatalysis activity of TNTAs in acid media by using metal doping. We believe the design of this electrocatalyst structure can be extended to obtain other metal-TNTA catalysts and make important developments in electrochemical fields to create promising, important ecological materials for environmental control.

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**Notes on contributor**

*Emran and Alanazi*, who are the corresponding authors, participated in the overall experiments. Both authors read and approved the final manuscript.

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