Enhanced Acidic Hydrogen Evolution on TiO2-Doped Gadolinium Electrocatalysts

Mohammed Alsawat*

Department of Chemistry, Faculty of Science, Taif University, Taif, Saudi Arabia.

1. Introduction

Water electrolysis is one of the key approaches used for producing CO2-free hydrogen. However, this electrochemical method involves a high electricity to smash the chemical links in the water molecule between oxygen and hydrogen, which makes it financially costly [1]. In order to minimize this expense, the process is conducted at elevated temperatures, but increasing the temperature is a further kind of energy consumption, so the researchers used catalysts to efficiently accelerate the reaction at room temperature to achieve a high hydrogen yield at lower costs [2].

2. Experimental Methods

2.1 Synthesis of Gd2O3-Doped TiO2 NPs

The TiO2-Gd1.0 and TiO2-Gd6.0 NPs were prepared following a previously reported method [9-14]. Briefly, titanium (IV) tert-butoxide [5.0 mL] was added to gadolinium(II) nitrate hexahydrate with two different atomic concentrations (1.0 and 6.0%) in DMSO (50 mL). The mixed solution was refluxed at 190 °C for 2 h. The obtained precipitate was collected by centrifuge (6000 rpm), washed several times with ethanol/acetone (2:1), and dried. Then, the obtained powders were calcinated at 400 °C for 2 h.

2.2 Characterizations of TiO2-Gd1.0 and TiO2-Gd6.0 NPs

The FT-IR spectra were recorded using Alpha-Atumated FT-IR spectrophotometer, Bruker in the range of 400-4000 cm-1. X-ray powder diffraction (XRD) has been carried out using a D8 Advance (Bruker, USA) X-ray diffractometer with CuKα operated at 40 kV and 40 mA. The program Xpert HighScore Plus (PANalytical, The Netherlands) was used to carry out the XRD pattern fitting of TiO2, TiO2-Gd1.0, and TiO2-Gd6.0 NPs [15]. This gives peak position (2θ), intensity (I), relative intensity (IR), half width (HW), etc. The Scherrer equation was used to estimate the crystallite size for each of the diffraction peaks, where the crystallite size was calculated as $d = k \lambda / W_{1/2} \cos \theta$ [16]. The constant k was taken equal to 0.9 and the used wavelength $\lambda = 1.54056$ Å then the average values were calculated. The least squares refinement method of Holland and Redfern was employed to retrieve unit cell constants from diffraction peak positions [17]. The morphology of the prepared samples was investigated using scanning electron microscopy (Hitachi S-4700 FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDX) and by using transmission electron microscope (Phillips CM200 TEM) operated at 200 kV. Simultaneous thermogravimetric analysis (TGA) coupled with differential thermal analysis (DTA) measurements were recorded using Shimadzu DTG 60H with system interface device in the atmosphere of nitrogen. The operational range of the instrument was from ambient temperature to 1000 °C at a heating rate of 10 °C min⁻¹.

2.3 Electrochemical Measurements

The working electrode (WE) employed in this work was a glassy carbon (GC) electrode loaded with a specific mass of the tested catalyst powder. The GC-loaded catalyst (WE) was prepared as follows. A mirror-like GC working electrode surface is first obtained via polishing with 0.3 µm alumina powder followed by 0.05 µm. It was then subjected to 20 minutes of ultrasonic washing using double-distilled water, and eventually dried into the air. Then, an aqueous dispersion (ink) of the catalyst (20 µL, 1.0 g/L) was drop-cast onto the electrode surface of GC. The GC-loaded catalyst (WE) was then left to dry in an oven at 100 °C for 30 min. A glassy carbon (GC) or graphite (Gr) as a counter electrode (CE) and a saturated calomel electrode (SCE) as a reference electrode (RE) have been used in all measurements.
mg/mL) was dropped onto the freshly polished, mirror-like, GC electrode, yielding a catalyst with a loading density of about 0.28 μg cm⁻².

The HER catalytic performance of the prepared nanocomposites was evaluated using a d.c. linear polarization technique, namely linear sweep voltammetry (LSV). In order to conduct an LSV experiment, the WE first cathodically (linearly) scanned with a potential sweep rate of 5.0 mVs⁻¹ starting from the corrosion potential (Ecorr).

In traditional electrochemical standard cell, electrochemical measurements have been conducted using Ag/AgCl and a long spiral Pt wires as the reference and counter electrodes. Potentials were measured against Ag/AgCl reference electrode, and then converted to the reversible electrode hydrogen (RHE) scale using the formula,

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} \]

where, pH = 0 and EAg/AgCl = 0.2046 V (25 °C). Measurements were performed at room temperature in a volume cell of 200 mL. An Autolab, Potentiostat/Galvanostat (PGSTAT30), was connected to the electrochemical cell to apply the LSV technique on the GC-catalyst/electrolyte interface. The test electrolyte was an aqueous solution of H₂SO₄ (0.5 M). Prior to use, the test solution was deoxygenated by Ar. The argon blanket has been kept on the solution during the entire experiment, to prevent convection effects. Repeating at least three measurements verified the strong reproducibility of the LSV and EIS findings. The average and standard deviation of the results have been estimated and reported.

3. Results and Discussion

3.1 Structural Analysis

The reaction of titanium(IV) tert-butoxide in presence of gadolinium(III) nitrate hexahydrate in boiling DMSO as solvent and oxidizing agent [9] produces the Gd³⁺-Ti(OH)₄ monomer. These hydroxo monomers were then reacted with the dimethyl sulfoxonium cation [18], which evolved from the degradation of DMSO molecules deposited at the surfaces of Gd³⁺-doped TiO₂ NPs. The formation of Ti(OH)₄ slows the growth of these NPs and prevents their agglomeration [19]. The FT-IR spectra of TiO₂-Gd₁.0 NPs before and after the calcination process are shown in Fig. 1.

Before annealing, the FT-IR spectrum of the synthesized precursor Gd³⁺-doped TiO₂ shows vibration bands in the region of 1000–1250 cm⁻¹, indicating the presence of tert-butoxy groups. Other two peaks at 1584 and 3383 cm⁻¹ can be attributed to H₂O bending and hydroxyl groups [20]. After annealing, the aforementioned peaks were not detected confirming the remove of all organic compounds from the samples by calcination.

The thermal decomposition of TiO₂-Gd₁.0 NPs before and after the calcination process is measured by simultaneous TGA-DTG-DTA in the range of 25–1000 °C. Before calcination, the TGA curve (Fig. 2a) displays three main steps. The first endothermic peak at 110 °C could be ascribed to the dehydration of adsorbed water molecules on the surface of TiO₂-Gd₁.0 NPs as well as the volatilization of the remaining organic solvent. The other two exothermic peaks at 250 and 510 °C were assigned to the degradation of organic moieties [21,22]. After calcination, no TGA weight losses are detected (Fig. 2b), confirming the high thermal stability of the prepared TiO₂-Gd₁.0 NPs.

Fig. 1 FT-IR spectra of TiO₂-Gd₁.0 NPs before (Black) and after calcination (Red)

The XRD pattern of TiO₂-Gd₁.0 NPs shows peaks at 2θ = 25.3°, 37.9°, 47.9°, 55.2°, 62.7°, 68.9°, and 75.2°, which correspond to the anatase crystallographic phase of TiO₂ [23-25]. The XRD patterns of TiO₂-Gd₅ and TiO₂-Gd₁₀ NPs show the same peaks positions with slight increment in the peaks' intensity which can be attributed to higher crystallinity. The anatase phase with the tetragonal lattice was refined in the space group I₄₁/aamd and [26] and dominated the composition of all TiO₂ samples. Table 1 shows the cell parameters and crystallite size of TiO₂, TiO₂-Gd₁₀, and TiO₂-Gd₁₀ NPs. The cell parameter a increases, which is due to the substitution of the Ti⁴⁺ by Gd³⁺ ions inside the TiO₂ lattice [27].

In order to investigate the morphology of the nanocomposites, SEM equipped with EDX was used. Fig. 4a shows the SEM of TiO₂-Gd₁.0 NPs as a representative example of Gd³⁺-doped TiO₂ NPs. It shows the presence of spherical particles (Gd₁.0) deposited on the surface of TiO₂ NPs. The composition of the nanocomposite was confirmed by the EDX, which shows the presence of Ti⁴⁺ and Gd³⁺ ions (Fig. 4b).

The morphology of TiO₂-Gd₁.0 was further investigated by transmission electron microscopy. It can be seen from the TEM images (Fig. 5) that the TiO₂-Gd₁.0 has a uniform size in quasi-spherical and cubic type particles. Upon doping TiO₂ with different concentrations of Gd³⁺, the average size was slightly increased.

Table 1 The cell parameters and crystallite size of TiO₂, TiO₂-Gd₁.0, and TiO₂-Gd₁₀ NPs

<table>
<thead>
<tr>
<th>NPs</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>D (nm)</th>
</tr>
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<tbody>
<tr>
<td>TiO₂</td>
<td>3.781(2)</td>
<td>9.414(6)</td>
<td>8(3)</td>
</tr>
<tr>
<td>TiO₂-Gd₁₀</td>
<td>3.785(2)</td>
<td>9.407(6)</td>
<td>10(3)</td>
</tr>
<tr>
<td>TiO₂-Gd₁₀</td>
<td>3.789(2)</td>
<td>9.408(6)</td>
<td>10(3)</td>
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Fig. 4 (a) SEM image and (b) EDX analysis of TiO$_2$-Gd$_{1.0}$ NPs

Fig. 5 (a) TEM and (b) HR-TEM images of TiO$_2$-Gd$_{1.0}$ NPs

3.2 HER Studies (LSV Measurements)

Fig. 6a represents the linear sweep voltammetry (LSV) curves, conducted at room temperature in 0.5 M H$_2$SO$_4$ solution at a potential scan rate of 5.0 mV s$^{-1}$, for the two synthesized catalysts, namely Gd$_{1.0}$/TiO$_2$ and Gd$_{6.0}$/TiO$_2$, in a comparison with bare GCE and TiO$_2$/GCE. The cathodic polarization data of Fig. 6a were fitted to Tafel equation, yielding the Tafel plots depicted in Fig. 6b, to extract the various electrochemical parameters of the HER associated with such cathodic polarization measurements.

![Tafel plots](image)

These HER electrochemical parameters, which include the exchange current density ($j_0$), Tafel slope ($\beta$), and the overpotential ($\eta$), the catalyst must acquire to generate a current density of 10 mA cm$^{-2}$, will be used to fully describe the kinetics of the HER on the surface of the tested catalysts. These parameters are listed in Table 2.

![Tafel plots](image)

Table 2

<table>
<thead>
<tr>
<th>Tested</th>
<th>Onset potential (E$_{onset}$, mV vs. RHE)</th>
<th>Tafel slope ($\beta$, mV dec$^{-1}$)</th>
<th>Exchange current density ($j_0$, mA cm$^{-2}$)</th>
<th>Overpotential at $j = 10$ mA cm$^{-2}$ (mV vs. RHE)</th>
</tr>
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<tr>
<td>bare GCE</td>
<td>-500 (12)</td>
<td>-266 (2.8)</td>
<td>3.90 (0.09) x 10$^5$</td>
<td>~500 (6.8)</td>
</tr>
<tr>
<td>TiO$_2$ NPs</td>
<td>-350 (6)</td>
<td>-160 (2)</td>
<td>5.5 (0.12) x 10$^4$</td>
<td>540 (6.8)</td>
</tr>
<tr>
<td>Gd$_{1.0}$/TiO$_2$</td>
<td>-95 (2.1)</td>
<td>-118 (1.6)</td>
<td>12 (0.2) x 10$^2$</td>
<td>390 (4.2)</td>
</tr>
<tr>
<td>Gd$_{6.0}$/TiO$_2$</td>
<td>-40 (0.9)</td>
<td>-33 (0.7)</td>
<td>25 (0.5) x 10$^2$</td>
<td>55 (1.1)</td>
</tr>
</tbody>
</table>

Being a well-known poor catalyst, the GCE is expected to exhibit very low catalytic activity for the HER. This is evidenced here from its highly negative onset potential for the HER, E$_{onset}$ (-500 mV vs. RHE), beyond which very little cathodic currents were generated, as shown in Fig. 6a, Curve 1. Compared to the bare GCE, the studied supporting material in this work, namely TiO$_2$/NPs (an n-type semiconductor material [28]) showed a considerable catalytic activity for the HER even in the dark [5,10,14].

The Tafel plot of the studied catalysts is shown in Fig. 6b. The Tafel slope ($\beta$) value of 2.34 RT/F for TiO$_2$-doped 1.0% Gd$^{3+}$ catalyst. This TiO$_2$-doped 1.0% Gd$^{3+}$ catalyst’s $j_0$ value is doubled when Gd$^{3+}$ percentage doping is increased from 1.0 to 6.0%.

The Tafel slope is another HER electrochemical kinetic parameter essentially employed to evaluate and compare the HER catalytic performance of the tested catalysts. Lower Tafel slopes reveal accelerated HER kinetics [32].

Classical theory [33-35] has shown that, in acidic aqueous media, the Tafel slopes values associated with the HER mechanisms proceeded by Volmer (Eq.1), Heyrovsky (Eq.2), and Tafel (Eq.3) were calculated to be approximately 200 mV dec$^{-1}$, 40 mV dec$^{-1}$ and 30 mV dec$^{-1}$, respectively.

H$_2$O$^+$ + e$^{-}$ + $\text{H}_2$O $\rightarrow$ H$_2$ (Volmer step) (1)

b = 2.34RT \alpha F

H$_2$O$^+$ + e$^{-}$ + $\text{SH}_\text{ads}$ $\rightarrow$ S + H$_2$O + H$_2$ (Heyrovsky) (2)

b = 2.34RT \alpha F

$\text{SH}_\text{ads}$ + $\text{SH}_\text{ads}$ $\rightarrow$ 2S + H$_2$ (Tafel step) (3)

b = 2.34RT \alpha F

where the $\text{SH}_\text{ads}$ denote the hydrogen atom adsorbed chemically on an active catalytic site (S). The pronounced diminution in the Tafel slope value from 168 mV dec$^{-1}$ for the TiO$_2$/GCE catalyst to 118 mV dec$^{-1}$ for TiO$_2$-doped 1.0% Gd$^{3+}$ catalyst and 33 mV dec$^{-1}$ for TiO$_2$-doped 6.0% Gd$^{3+}$ catalyst ranks this catalyst among the best HER electrocatalysts ever reported in the literature as well as in our lab [36, 37] for the commercial Pt/C catalyst (~30 mV dec$^{-1}$) under the same operating conditions. These results present Volmer-Tafel steps and Eq.(1) and (3); with the recomposition (Tafel) step.
being the rate limiting [35], as the possible mechanism for the HER over the tested catalysts.

The tight chemical coupling between the supporting material, namely TiO₂ NPs and the doped Gd NPs may be one of the major reasons behind the high HER catalytic performance of the two studied TiO₂-doped Gd²⁺ catalysts. This high chemical interaction results in the formation of highly sparse (aggregation-free) metal NPs selectively growing on the surface of TiO₂, and the existence of such doped Gd NPs, whose population is significantly enhanced with its doping percentage, in the TiO₂ crystal lattices expected to provide the HER with abundant active catalytic sites. It is believed that each supported (even doped) metallic NP can be viewed as a nanoelectrode or even a proton reducing nanocathode [36]. Another explanation for its increased catalytic activity against the HER may be the large electrochemical surface area of such catalysts caused by the high specific surface area of the supporting material (TiO₂ NPs). The catalytic performance was found to improve with increase in doped Gd²⁺ content in the nanocomposite. This is evidenced from the two essential HER electrochemical kinetic parameters, namely jₖ
total and j₈, employed to evaluate and compare the HER catalytic activity of the compared electrocatalysts.

4. Conclusion

Gadolinium-doped TiO₂ NPs, namely TiO₂-Gd₁₀ and TiO₂-Gd₂₀ were fabricated and fully characterized using FTIR, TGA-DTA, XRD, SEM and TEM. XRD investigations showed that Ti₄⁺ was properly substituted by Gd³⁺ in the TiO₂ host lattice. The two synthesized TiO₂ NPs-doped Gd²⁺ exhibited remarkable catalytic activity towards the HER in sulphuric acid solution (0.5 M). The catalytic performance was found to improve with increase in doped Gd²⁺ content in the nanocomposite. This is evidenced from the two essential HER electrochemical kinetic parameters, namely jₖ
total and j₈, employed to evaluate and compare the HER catalytic activity of the compared electrocatalysts. The TiO₂-Gd₁₀ catalyst consumed an overpotential of η₀ = 55 mV to deliver a current density of 10 mA cm⁻². On the other hand, the TiO₂-Gd₂₀ acquired much higher overpotential (η₀ = 290 mV) to achieve the same current. Also, the TiO₂-Gd₂₀ catalyst recorded a j₈ value (0.25 mA cm⁻²) as twice as that calculated for the TiO₂-Gd₁₀. These findings indicated that the TiO₂-Gd₁₀ catalyst is more catalytically active than the TiO₂-Gd₂₀ catalyst.

References