Enhanced Acidic Hydrogen Evolution on TiO$_2$-Doped Gadolinium Electro catalysts

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ABSTRACT

Gadolinium-doped TiO$_2$ NPs, namely TiO$_2$:Gd$_{1.0}$ and TiO$_2$:Gd$_{6.0}$ have been synthesized using two different atomic concentrations of gadolinium(III) nitrate hexahydrate in presence of titanium(IV) tert-butoxide as a titanium precursor and dimethyl sulfoxide as a solvent. The structure and morphology of these NPs have been characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric-differential thermal analysis (TGA-DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The two synthesized TiO$_2$:Gd$_{1.0}$ and TiO$_2$:Gd$_{6.0}$ NPs were tested as electrocatalysts for hydrogen evolution reaction (HER) in an acidic electrolyte (0.5 M H$_2$SO$_4$) based on linear sweep voltammetry (LSV) measurements. LSV data were fitted to Tafel equation and the various electrochemical parameters describing the HER kinetics were evaluated and discussed. Results demonstrate that the kinetics of the HER on the surface of TiO$_2$ NPs significantly enhanced upon doping it with Gd$^{3+}$, proportionally to the atomic concentration of the Gd$^{3+}$ cations in the TiO$_2$ NPs.

1. Introduction

Water electrolysis is one of the key approaches used for producing CO$_2$-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].

Literature reported a huge number of newly synthesized materials for the electrochemical production of hydrogen from various aqueous media with a wide range of pH [3]. Most of them, particularly the most efficient ones, are unstable and expensive. Literature also revealed an intense shortage of information on TiO$_2$ NPs-doped rare earth ions in electrocatalysis applications [4,5]. The Fermi level of TiO$_2$ is higher than that of gadolinium and accordingly the excited electrons of the TiO$_2$ are transferred to gadolinium deposited on its surface. Therefore, the probability of electron-hole recombination is limited leading to efficient separation of charges [6]. Moreover, rare earth elements featuring 4f electronic configuration and hence are very suitable dopants for adjusting properties of TiO$_2$. Among the rare earth elements, neodymium and gadolinium are commonly used dopants for different applications [7].

Recently, workers including my group studied the role of palladium and europium on TiO$_2$ performance and they have obtained a positive effect towards the catalysis of the hydrogen energy reaction (HER) [5-8].

This work aims to generate a hydrogen gas with high efficiency at room temperatures using safe, inexpensive, and easily prepared new materials. Among the rare earth elements, neodymium and gadolinium are commonly used dopants for different applications [7].

2. Experimental Methods

2.1 Synthesis of Gd$^{3+}$-Doped TiO$_2$ NPs

The TiO$_2$:Gd$_{1.0}$ and TiO$_2$:Gd$_{6.0}$ 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 calcined at 400 °C for 2 h.

2.2 Characterizations of TiO$_2$:Gd$_{1.0}$ and TiO$_2$:Gd$_{6.0}$ NPs

The FT-IR spectra were recorded using Alpha-Antunated 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 TiO$_2$, TiO$_2$:Gd$_{1.0}$ and TiO$_2$:Gd$_{6.0}$ 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 $d = kλ/WHC_{os}$ [16]. The constant k was taken equal to 0.9 and the used wavelength $λ_{CuKα}$ = 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 peaks position [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 (Philips 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
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 mV/s 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,

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

where, pH = 0 and \( E_{\text{Ag/AgCl}} = 0.2046 \) 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 deaerated through 30 minutes of purging with 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 Gd₄TiO₄OH monomer. These hydroxide monomers were then reacted with the dimethyl sulfoxonium cation [18], which evolved from the degradation of DMSO molecules deposited at the surfaces of Gd₄-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-Gd₃.0 NPs before and after the calcination process are shown in Fig. 1.

Before annealing, the FT-IR spectrum of the synthesized precursor Gd₄-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 removal of all organic compounds from the samples by calcination.

![Fig. 1 FT-IR spectra of TiO₂-Gd₃.0 NPs before (Black) and after calcination (Red)](image)

The thermal decomposition of TiO₂-Gd₃.0 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-Gd₃.0 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-Gd₃.0 NPs.

![Fig. 2 TGA-DTG-DTA curves of TiO₂-Gd₃.0 NPs recorded in the range of 25–1000 °C a) before and b) after calcination](image)

The XRD patterns of TiO₂, TiO₂-Gd₁.0 and TiO₂-Gd₃.0 NPs fitted using Xpert HighScore Plus (Fig. 3). The XRD pattern of TiO₂ 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-Gd₁.0 and TiO₂-Gd₃.0 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/amd I₄₁/amd [26] and dominated the composition of all TiO₂ samples. Table 1 shows the cell parameters and crystallite size of TiO₂, TiO₂-Gd₁.0, and TiO₂-Gd₃.0. The cell parameter a increases, which is due to the substitution of the Ti⁴⁺ by Gd³⁺ ions inside the TiO₂ lattice [27].

![Fig. 3 XRD patterns where the black circles are the observed data and the red solid line is the calculated profile of TiO₂, TiO₂-Gd₁.0 and TiO₂-Gd₃.0 NPs](image)

| NPs     | a (Å) | c (Å) | D (nm) |
|---------|-------|-------|--------|
| TiO₂    | 3.781(2) | 9.414(6) | 8(3)   |
| TiO₂-Gd₁.0 | 3.785(2) | 9.407(6) | 10(3)  |
| TiO₂-Gd₃.0 | 3.789(2) | 9.408(6) | 10(3)  |

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.
The Tafel slope is another HER electrochemical kinetic parameter and the overpotential ($\eta$) the higher its catalytic activity. From Table 2, the $\eta$ value decreases following the sequence: TiO$_2$ (540 mV) < TiO$_2$-doped 1.0% Gd$^{3+}$ (290 mV) < TiO$_2$-doped 6.0% Gd$^{3+}$ (55 mV). These results present TiO$_2$-doped 6.0% Gd$^{3+}$ as the best performing electrocatalyst.

Such reduced values of $E_{onset}$ and $\eta$ favor H$_2$ generation at lower overpotentials resulting in higher $j_\text{cell}$ values. Data in Table 2 confirmed that; the value of $j_\text{cell}$ is considerably increased (~2.2 times) from 5.5 × 10$^3$ mA cm$^{-2}$ for TiO$_2$-doped alone (i.e., without doping) to 12 × 10$^3$ mA cm$^{-2}$ for TiO$_2$-doped 1.0% Gd$^{3+}$ catalyst. This TiO$_2$-doped 1.0% Gd$^{3+}$ catalyst's $j_\text{cell}$ 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 slope values associated with the HER mechanisms proceeded by Volmer (Eq.1), Heyrovsky (Eq.2) and Tafel (Eq.3) were calculated to be approximately 120 mV dec$^{-1}$, 40 mV dec$^{-1}$ and 30 mV dec$^{-1}$.

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

$$b = \frac{2.34RT}{aF} \equiv 120 \text{ mV} \text{dec}^{-1}$$

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

$$b = \frac{2.34RT}{2F} \equiv 40 \text{ mV} \text{dec}^{-1}$$

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

$$b = \frac{2.34RT}{(1 + a)}F \equiv 30 \text{ mV} \text{dec}^{-1}$$

where the $\text{SH}_\text{ads}$ denote the hydrogen 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 the kinetics of the HER over studied catalysts as: TiO$_2$/GCE < TiO$_2$-doped 1.0% Gd$^{3+}$ < TiO$_2$-doped 6.0% Gd$^{3+}$. These results confirm the catalytic impact of the doped Gd$^{3+}$ on the HER kinetics on TiO$_2$ NPs.

The best catalyst here, namely TiO$_2$-doped 6.0% Gd$^{3+}$ recorded a small Tafel slope value of 33 mV dec$^{-1}$, which is close to that 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, Eqs.(1) and (3), with the recombination (Tafel) step

| Tested cathode | Onset potential ($E_{onset}$, mV vs. RHE) | Tafel slope ($\beta$, mV dec$^{-1}$) | Exchange current density ($j_\text{cell}$, mA cm$^{-2}$) | Overpotential ($\eta$, mV) |
|---------------|----------------------------------------|-------------------------------------|---------------------------------|--------------------------|
| bare GCE      | -500(12)                               | -266(2.8)                           | 3.98(0.09) × 10$^5$             |                          |
| TiO$_2$ NPs   | -350(6)                                | -160(2)                             | 5.5(0.12) × 10$^5$              | 540(6.8)                 |
| Gd$_{1.0}$/TiO$_2$ | -95(2.1)                         | -118(1.6)                           | 12.0(2.0) × 10$^2$             | 290(4.2)                 |
| Gd$_{6.0}$/TiO$_2$ | -40(0.9)                          | -33(0.7)                            | 25.0(5.0) × 10$^2$             | 55(1.1)                  |

The best catalyst here, namely TiO$_2$-doped 6.0% Gd$^{3+}$ recorded a small Tafel slope value of 33 mV dec$^{-1}$, which is close to that 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, Eqs.(1) and (3), with the recombination (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 TiO$_2$ NPs and the doped Gd NPs may be one of the main reasons behind the high HER catalytic performance of the two studied TiO$_2$-doped Gd$^3+$ catalysts. This high chemical interaction results in the formation of highly sparse (aggregation-free) metal NPs selectively growing on the surface of TiO$_2$, and the existence of such doped Gd NPs whose population is significantly enhanced with its doping percentage, in the TiO$_2$ 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 high surface area of such catalysts caused by the high specific surface area of the supporting material (TiO$_2$ NPs: 136.67 m$^2$/g [M4]) itself. In fact, high-specific surface area substrates allow a good dispersion of the supported NPs with significantly reduced size. This, in turn, boosts the exposure of more active HER sites [36].

4. Conclusion

Gadolinium-doped TiO$_2$ NPs, namely TiO$_2$-Gd$_{1.0}$ and TiO$_2$-Gd$_{6.0}$ were fabricated and fully characterized using FTIR, TGA-DTA, XRD, SEM and TEM. XRD investigations showed that Ti$^{4+}$ was properly substituted by Gd$^{3+}$ in the TiO$_2$ host lattice. The two synthesized TiO$_2$ NPs-doped Gd$^{3+}$ 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 Gd$^{3+}$ content in the nanocomposite. This is evidenced from the two essential HER electrochemical kinetic parameters, namely $j_0$ and $n$, and employed to elucidate the HER catalytic activity of the compared catalysts by the two synthesized TiO$_2$ NPs-doped Gd$^{3+}$ catalysts in comparison to the TiO$_2$-Gd$_{1.0}$ catalyst.

These findings indicate that TiO$_2$-Gd$_{1.0}$ catalyst is more catalytically active than the TiO$_2$-Gd$_{6.0}$ catalyst.

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