



Exploring the role of rare earth elements doped TiO₂ based photoanodes on the performance of dye-sensitized solar cells

Berrak Caliskan¹ · Enes Sayan¹ · Erdal Igman²

Received: 20 June 2025 / Accepted: 11 February 2026 / Published online: 24 March 2026
© The Author(s) 2026

Abstract

This study investigates the synthesis and characterization of rare earth elements (REEs) doped TiO₂ thin films based photoanodes for use in dye-sensitized solar cells (DSSCs). For this purpose, TiO₂ films were doped with Ho³⁺, La³⁺, Er³⁺, and Yb³⁺ ions to enhance photoelectrochemical properties. Characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy, BET surface area analysis, and X-ray photoelectron spectroscopy (XPS) were employed for the structural, morphological, and optical characterization of the synthesized photoanodes and CEs. REEs doping improved the surface morphology and optical properties of TiO₂, in particular, it increased photon absorption in the visible light range. La³⁺ and Ho³⁺ significantly improved photovoltaic performance, achieving power conversion efficiencies of 3.78% and 2.87%, respectively, compared to that of pure TiO₂. These enhancements indicate improved charge transport and light harvesting due to incorporation of REEs. Additionally, replacing the conventional platinum counter electrode (CE) with reduced graphene oxide (rGO) further enhanced performance, offering a low-cost and efficient alternative. The study highlights the combined benefits of REEs doping and rGO integration in improving DSSCs efficiency. These findings contribute to the development of more sustainable, cost-effective solar energy technologies and underline the potential of REEs-doped TiO₂ films and rGO electrodes in advancing next-generation photovoltaic devices.

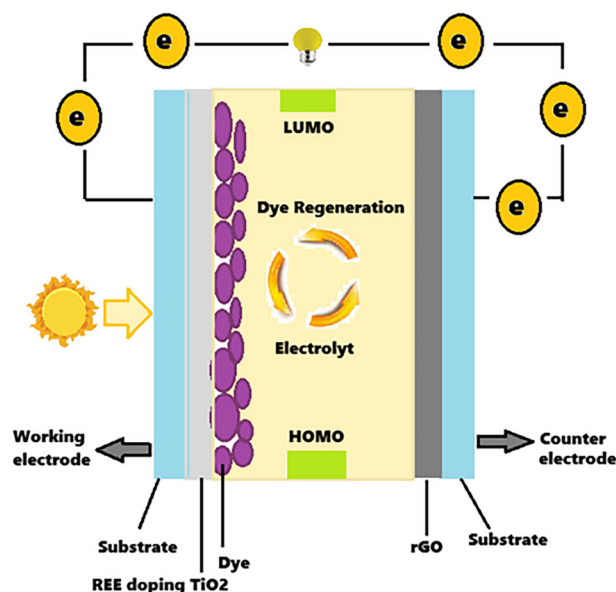
Supplementary information The online version contains supplementary material available at <https://doi.org/10.1007/s10971-026-07134-y>.

✉ Berrak Caliskan
berrak.c@atauni.edu.tr

¹ Atatürk University, Faculty of Engineering, Department of Chemical Engineering, Erzurum, Turkey

² Bayburt University, Department of Material Science and Nanotechnology Engineering, Bayburt, Turkey

Graphical Abstract



Keywords DSSCs · Photovoltaic Performance · Rare Earth Elements Doping · rGO · TiO₂

Highlights

- Doping with REE (Ho³⁺, La³⁺, Er³⁺, and Yb³⁺) enhanced light absorption, raising efficiency up to 3.78%.
- rGO outperformed platinum as a low-cost, highly conductive counter electrode.
- Doping narrowed the bandgap and increased surface area, boosting dye loading and light harvesting.
- UV-Vis, EIS, and IPCE analyses showed better charge transport and lower recombination, especially in 1.0% Ho³⁺-N-rGO cells.

1 Introduction

Climate change, driven by global warming, can severely disrupt ecosystem balance. For this reason, it is essential to develop sustainable energy solutions to prevent damage to the environment [1]. Solar energy, which is among the sustainable energy sources, is an economical, environmentally friendly green energy source. Dye-Sensitized Solar Cells (DSSCs), which are part of photovoltaic technology converting solar energy directly into electricity, have recently become one of the most promising solar cells of the third generation [2]. Since their introduction by O'Regan and Grätzel in 1991, DSSCs have been an important area of research among solar energy conversion technologies due to their low manufacturing costs, flexibility, and potential for high efficiency [3, 4]. Compared to other thin film solar cells, DSSCs can also operate in diffused light and cloudy weather. Among the green technologies, DSSCs provide sustainable energy with low or zero greenhouse gas emissions, support economic development, and reduce fossil fuel dependency. They also provide job opportunities and

electricity access in developing countries [5]. These features of DSSCs make it a promising option for large-scale energy production and also give them an important position in the future of renewable energy [1, 6, 7].

DSSCs typically consist of a nanocrystalline metal oxide photoanode, a dye (organic or synthetic dyes), a redox electrolyte (most commonly I₃⁻/I⁻), and a CE, usually Pt-coated FTO [5, 8, 9]. One of the most important elements determining the power conversion efficiency (PCE) in DSSCs is the photoanode, because it plays an active role in both the generation and separation of charges. In addition, the diffusion resistance in the photoanode is one of the critical factors determining the PCE of solar cells. In this context, it has great potential to accelerate electron transport and facilitate higher dye loading by carefully designing semiconductor films and optimizing their morphology [7, 10]. TiO₂ is a widely used photoanode material in DSSCs due to its wide band gap, chemical stability and high electron mobility. TiO₂ P25 based photoanodes have become an important choice in DSSCs devices due to their improved optoelectric properties [11, 12]. Many methods

are commonly used in the synthesis of TiO_2 , such as the sol-gel method [13], hydrolysis [14], spray pyrolysis [15], atomic layer deposition [16] and hydrothermal method [17]. Among these methods, the sol-gel method has many advantages, such as simple equipment requirements, high product purity, insensitivity to environmental conditions during preparation, and good quality and homogeneity of the coated product [18–20].

TiO_2 has been the subject of extensive research due to its electrical, optical, and chemical properties. This occurs because for most dye molecules, the photon-excited energy level (LUMO) lies above the conduction band edge of TiO_2 , allowing electrons to be efficiently injected into the conduction band of TiO_2 [21]. However, disadvantages of TiO_2 , such as its low absorption capacity in the visible light spectrum and its sensitivity to electron-hole recombination, motivate investigations into new materials and composites to improve the efficiency of DSSCs [1, 8]. Utilizing REEs to improve the optical performance of optoelectronic materials has been an important research topic for a long time. By deliberately adding impurities to the TiO_2 lattice through the doping process, it can effectively change its electronic properties [22]. It is known that DSSCs can be effectively used in the ultraviolet (UV) and near-infrared (NIR) regions beyond the visible region by doping REEs with 4f electronic transitions. REEs contribute to the activation of UV and IR regions in DSSCs through up-conversion (UC) and down-conversion (DC) mechanisms. Through luminescence conversion processes including UC and DC, REEs can increase light harvesting and improve PCE by converting UV or NIR photons into visible light [23, 24]. Utilizing REEs to improve the optical performance of optoelectronic materials has been an important research topic for a long time. Therefore, the addition of REEs to the TiO_2 semiconductor material in solar cells provides a significant improvement in the cell performance [25, 26]. In the study conducted by Miao et al. (2015), In_2O_3 , $\text{In}_2\text{O}_3:\text{Dy}^{3+}$, $\text{In}_2\text{O}_3:\text{Ho}^{3+}$, and $\text{In}_2\text{O}_3:\text{Er}^{3+}$ nanotubes were prepared via electrospinning. It was reported that doping with REEs caused an increase in J_{SC} value compared to the undoped cell. PEC values for In_2O_3 , $\text{In}_2\text{O}_3:\text{Dy}^{3+}$, $\text{In}_2\text{O}_3:\text{Ho}^{3+}$, and $\text{In}_2\text{O}_3:\text{Er}^{3+}$ cells were measured as 0.5, 1.1, 1.1, 1.4, respectively [27]. In another study, Arslan (2018) synthesized pure, 0.5% M and 1.0% M Eu^{3+} doped TiO_2 photoanode in DSSCs by sol-gel method. As a result, it was observed that the efficiency value increased by 27.2% in the cell doped with 1.0% M Eu^{3+} was doped compared to the pure cell using Pt in the CE [28]. In another study, Khanam et al. (2017), PEO/c-MWCNT/PAni gel electrolyte and $\text{Ce}^{3+}@\text{TiO}_2$ nanoparticles were synthesized by in situ polymerization and hydrothermal methods, respectively. DSSCs were prepared using PEO/c-MWCNT/PAni gel electrolyte and Ce^{3+} -doped TiO_2 nanoparticles as

photoanodes. The highest efficiency of 4.08% was obtained with 0.5 wt% $\text{Ce}^{3+}@\text{TiO}_2$. This provided a 60% efficiency increase compared to pure TiO_2 as the photoanode. Furthermore, this improvement was interpreted as the decrease in the energy of the optical band gap and more efficient electron injections from the dye [29]. In the study of Farheen et al. (2017), doping of Eu in TiO_2 at atomic level was carried out by sol-gel method and DSSCs were produced by conventional method (Pt in cathode, N719 dye). The yield was 0.54% with pure TiO_2 , 0.9% with 50 μg Eu addition, and 1.01% with 400 μg Eu addition. The effect of Eu concentration showed that the increase in J_{SC} value provided an improvement in cell parameters by improving photocurrent and electronic conduction [30].

The REEs ions enable the UC process via 4f-4f transitions, and this process generates strong emission lines, offering high photostability along with long UC luminescence lifetime ($\sim\text{ms}$) [31]. In their study, Markose et al. (2023) investigated the effect of Gadolinium doping on TiO_2 and found that it improved the TiO_2 surface area, increased light absorption, facilitated charge transport at optimum concentration, and reduced recombination [32]. Therefore, incorporating REEs into the DSSCs photoanode has proven to be a promising strategy to increase efficiency by enhancing charge transport pathways, reducing charge recombination, improving light scattering and photon utilization, and broadening spectral absorption via luminescence conversion.

According to the International Energy Agency (IEA), it is important to reduce production costs by expanding the use of natural resources [33]. Natural pigments are considered a promising alternative for DSSCs production due to their widespread availability, non-toxicity, low cost, and environmentally friendly nature [34, 35]. Natural pigments, including betalains, carotenoids, anthocyanins, and chlorophyll, are widely used in cell production today and are mostly obtained from plants, especially from parts such as fruits, flowers, leaves, seeds, roots, and wood. However, the PCE of DSSCs sensitized with natural dyes has not yet reached the desired level [17]. In DSSCs applications, vegetal dyes containing anthocyanins in red, purple, and blue tones stand out. Because the carboxyl and hydroxyl groups in their structures form a strong bond with TiO_2 [36]. Studies using sensitizers obtained from the Hibiscus plant containing anthocyanin have been reported in previous studies [37–41].

In DSSCs, CE, high electronic conductivity, low charge transfer resistance, and high catalytic activity at the CE/electrolyte interface are among the electrical properties required [42]. Carbon-based materials are preferred as CE due to their low cost. There are many carbon-based materials such as activated carbon, volcanic carbon, carbon nanotube (CNT), multi-walled carbon nanotube (MWCNT),

and graphene. Thanks to its ability to improve electron transport, two-dimensional graphene sheets provide offer advantages in photovoltaic materials [43]. Recently, intensive research are being carried out on graphene structures, which can be used instead of Pt as cathode material to increase efficiency and reduce charge transfer resistance (R_{ct}), due to their mechanical strength, high conductivity, low-cost production material, and high specific surface area [43–47]. In one of their studies, Mao et al. [48] fabricated DSSCs using reduced graphene oxide (rGO) synthesized by the Hummers method as CE, a TiO_2 photoanode prepared by the screen-printing method. N-719 dye was used as the sensitizer, and an electrolyte solution consisting of 0.50 mol LiI , 0.10 mol 4-tertbutylpyridine, 0.05 mol I_2 , and acetonitrile-propenyl carbonate. The PEC value obtained for this cell was as 1.66% [48]. In another study, Gemeiner et al. [49] designed DSSCs using TiO_2 photoanode prepared by screen printing method, N-719 dye as sensitizer, graphene oxide (GO) prepared by spin-coating method and rGO obtained by plasma reduction at the CE. V_{OC} (V), J_{SC} (mA/cm^2), FF and η (%) values for two cells using GO and rGO in the CE were 0.46, 3.58, 0.27, 0.44; 0.55, 7.20, 0.29, 0.89, respectively. The main reason for the low efficiency was found to be that hydrogen plasma reduction significantly reduced the presence of carbon-oxygen bonds, while water-based GO dispersion significantly reduced the sp^3 hybridization areas in rGO layers formed by spin coating method. In addition, it was reported that plasma reduction reduced the electrical sheet resistance of rGO electrodes [49]. In this study, GO and rGO synthesized using the Hummers method were used to produce nanocomposites with polyvinylpyrrolidone (PVP). PVP is an ideal polymer for various applications due to its non toxicity, chemical stability, and superior optical, electrical, and mechanical properties. It is a well defined synthetic polymer with long chains of N-vinylpyrrolidone monomers. It copolymerizes with other polymers, enabling the development of novel nanocomposite films.

In this study, TiO_2 synthesized via the sol-gel method was doped with Ho^{3+} , La^{3+} , Er^{3+} and Yb^{3+} ions at certain concentrations. In addition to the widely used commercially available N719 dye, natural dye derived from the Hibiscus plant was employed as an alternative dye sensitizer. The CE was prepared using GO and rGO materials synthesized by the Hummers method and applied onto fluorine doped tin oxide (FTO) conductive substrates using the Doctor Blade technique. Finally, the prepared DSSCs were subjected to performance analysis.

2 Experimental

2.1 Materials

FTO substrate and N-719 ($\text{C}_{58}\text{H}_{86}\text{N}_8\text{O}_8\text{RuS}_2$) dye used in this study were supplied by Sigma-Aldrich. The hibiscus

flowers used in the experiments were obtained from a local herbalist. Graphite powder, sodium dodecyl sulfate (SDS, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$), sulfuric acid (H_2SO_4), dimethylformamide (DMF, Merck), sodium nitrate (NaNO_3), polyvinylpyrrolidone (PVP, $(\text{C}_6\text{H}_9\text{NO})_n$ Sigma-Aldrich), hydrogen peroxide (H_2O_2 , Isolab), and potassium permanganate (KMnO_4 , Merck) were used for CE synthesis. 1-Butyl-3-methylimidazolium iodide ($\text{C}_8\text{H}_{15}\text{IN}_2$) (Sigma-Aldrich), 3-methoxypropionitrile ($\text{C}_4\text{H}_7\text{NO}$) (Sigma-Aldrich), 4-tert-butylpyridine ($\text{C}_9\text{H}_{13}\text{N}$) (Acros Organics), iodine (I_2 , Isolab), and lithium iodide hydrate ($\text{LiI} \cdot x\text{H}_2\text{O}$) (Acros Organics) were used in the preparation of the electrolyte. Acetic acid, TiO_2 powder (Sigma-Aldrich), Titanium (IV) tetraisopropoxide (TTIP), Erbium (III) nitrate pentahydrate, Lanthanum (III) nitrate hexahydrate (Acros Organics), Holmium (III) nitrate pentahydrate (Alfa Aesar), Ytterbium (III) nitrate hydrate- $\text{N}_3\text{O}_9\text{Yb}$ (abcr), P25 (Degussa), Triton-X 100 (Afg Bioscience LLC), and Ethanol (Isolab) were used for the preparation of the photoanode.

2.2 Synthesis of pure and doped TiO_2 solutions by sol-gel method (preparation of photoanode)

In this study, pure and doped TiO_2 were synthesized in two stages. The first stage, 1.7 mL of TTIP was mixing with ethanol. In the second stage, 8 mL of ethanol and 3 mL of acetic acid were added drop wise to the mixture prepared in the first stage. For the synthesis of doped TiO_2 , the amount of the dopant was determined as % M and added to the mixture. After homogenization, the mixture was allowed to rest for 48 h. For the preparation of the TiO_2 paste, 0.5 mL of rested synthesis, 0.25 g of P25 TiO_2 powder, 0.5 mL of acetic acid, and a few drops of Triton-X 100 were mixed. The resulting TiO_2 paste was applied to the cleaned FTO substrate using the ‘Doctor Blade’ technique and calcined at 500°C for 1 h. Figure 1 shows the procedure for preparing the TiO_2 paste via the sol-gel method.

2.3 Preparation of GO and rGO

GO was synthesized using the Hummers method. 3 g of graphite powder, 69 mL of sulfuric acid, and 1.5 g of NaNO_3 were mixed. When the solution temperature reached 0°C in an ice bath, 9 g of KMnO_4 was added. Subsequently, 138 mL of de-ionized water was added, and the solution was stirred at 98°C for 15 min, followed by another 480 mL of de-ionized water. A constant temperature circulator was used to maintain the 98°C temperature. Oxidation was completed by adding 30% H_2O_2 until the color of the solution changed from brown to yellow. GO was washed with de-ionized water until the pH value became 7, then filtered and dried at 60°C . rGO was

Fig. 1 TiO₂ paste preparation procedure by sol-gel method

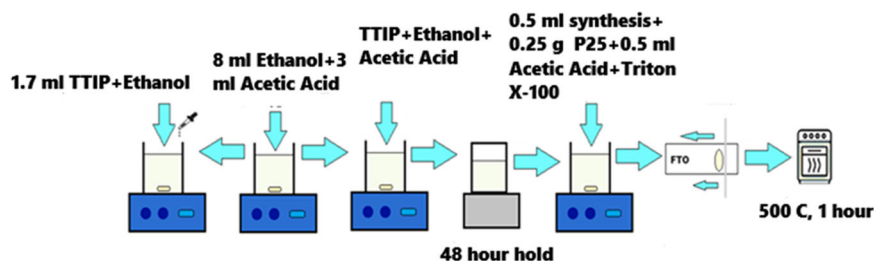
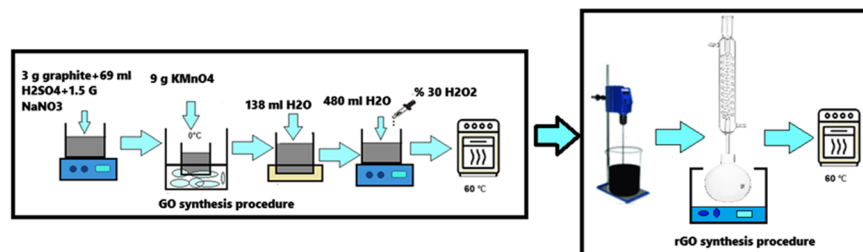


Fig. 2 Preparation procedure of GO and rGO



dissolved in 400 mL of DMF with 0.8 g of GO powder and subjected to reflux for 6 h. Finally, the solution was filtered and washed with ethanol and de-ionized water, and dried at 60 °C [50]. The preparation procedure of GO and rGO is illustrated in Fig. 2.

2.4 Preparation of CE

In total, 0.44 g of the synthesized GO and rGO were ultrasonically dispersed in 20 mL of deionized water containing 1.0% (w/w) SDS for 1 h. SDS, a surfactant was used to improve the dispersion of rGO in water and enhance its adhesion to the FTO substrate. During the preparing of GO-PVP and rGO-PVP thin films, 1.0% (w/w) PVP (C₆H₉NO)_n was added to prevent re-agglomeration of graphene, and the mixture was stirred for an additional hour. The GO-PVP and rGO-PVP paste was dried in a controlled manner at 50 °C, applied onto the cleaned FTO surface using the ‘Doctor Blade’ method, and annealed at 350 °C for 15 min [51].

2.5 Preparation of electrolyte

A liquid electrolyte was employed in DSSCs. The electrolyte solution was prepared by dissolving 0.1 M 4-tert-butylpyridine, 0.6 M 1-butyl-3-methylimidazoium iodide, 0.01 M iodine, and 0.1 M lithium iodide hydrate in 3-methoxypropionitrile solvent and then stirred for 2 h.

2.6 Preparation of N-719 and hibiscus dyes

The N-719 dye solution was prepared by stirring in 5×10^{-4} Methanol for 1 h. Hibiscus leaves were washed with deionized water to remove dust and dirt and then dried. The leaves were ground in a blender to reduce their size. Dye

molecules were extracted from the hibiscus leaves using solvent extraction (cold maceration). 2 g of hibiscus leaves were added to 20 mL of ethanol and left to stand for 24 h, followed by filtration through filter paper. Finally, the extract was concentrated to 6 mL in an oven at 60 °C, and the dye solution was kept for 24 h prior to incorporation into the photoanodes [52].

2.7 Preparation of solar cells

The liquid electrolyte was dropped onto the surfaces of pure and REEs doped photoanodes sensitized with N-719 and hibiscus dyes which were then assembled with the CE surfaces coated with GO and rGO in a sandwich configuration, facing each other. The properties of the DSSCs prepared in this study are summarized in Table 1.

2.8 Characterization

The structural, morphological and optical characterization of the synthesized photoanodes and CEs were analyzed using scanning electron microscopy (SEM) (Zeiss Sigma 300), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) (PANalytical Empyrean), X-ray photoelectron spectroscopy (XPS) (SPCES-Flex), surface area measurement (BET), Raman spectroscopy (WITech Alpha 300 R), (Malvern Zetasizer Nano ZSP), UV-visible absorption spectroscopy (Shimadzu UV-3600 Plus) located at Atatürk University Eastern Anatolian High Technology Application and Research Center (DAYTAM). Analyses of the prepared N-719 and Hibiscus sensitizers were carried out by Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer SPCEtrum One) and UV-visible absorption spectroscopy.

Table 1 Properties of undoped and REE doped DSSCs synthesized by sol-gel method in photo-anode using TiO_2

Cell No	Cell Code	Photoanode	Dye	Photocathode
1	TiO_2 -N-GO	TiO_2	N-719	GO
2	TiO_2 -H-GO	TiO_2	Hibiscus	GO
3	TiO_2 -N-rGO	TiO_2	N-719	rGO
4	TiO_2 -H-rGO	TiO_2	Hibiscus	rGO
5	0.5 Ho TiO_2 -N-rGO	%0.5 M Ho TiO_2	N-719	rGO
6	1.0 Ho TiO_2 -N-rGO	%1.0 M Ho TiO_2	N-719	rGO
7	1.5 Ho TiO_2 -N-rGO	%1.5 M Ho TiO_2	N-719	rGO
8	1.0 Ho TiO_2 -H-rGO	%1.0 M Ho TiO_2	Hibiscus	rGO
9	0.5 Er TiO_2 -N-rGO	%0.5 M Er TiO_2	N-719	rGO
10	1.0 Er TiO_2 -N-rGO	%1.0 M Er TiO_2	N-719	rGO
11	1.5 Er TiO_2 -N-rGO	%1.5 M Er TiO_2	N-719	rGO
12	1.0 Er TiO_2 -H-rGO	%1.0 M Er TiO_2	Hibiscus	rGO
13	1.0 La TiO_2 -N-rGO	%1.0 M La TiO_2	N-719	rGO
14	1.0 La TiO_2 -H-rGO	%1.0 M La TiO_2	Hibiscus	rGO
15	1.0 Yb TiO_2 -N-rGO	%1.0 M Yb TiO_2	N-719	rGO
16	1.0 Yb TiO_2 -H-rGO	%1.0 M Yb TiO_2	Hibiscus	rGO

Performance tests of DSSCs with an active cell area of 0.196 cm^2 were conducted with the Keithley 2400 device. Current-voltage (I–V) curves were recorded under applied voltage. Performance evaluations were made with HelioSim CL60 solar simulator under 100 mW/cm^2 illumination conditions using AM 1.5 G standard filter. Using these data, Current Density (J_{SC}), Open Circuit Voltage (V_{OC}), Fill Factor (FF), Maximum Power (P_{MAX}), and PCE (η) were calculated. The potentiostat/galvanostat (Gamry PCI14/750) used in EIS measurements were performed using a 10 mV AC signal in the frequency range of 10^{-2} – 10^5 Hz . Nyquist diagrams were simulated with an appropriate equivalent circuit model in the software of the device. The resistance values of the elements in the equivalent circuit model were determined as a result of the analysis performed with EC-Lab software. The incident photon-to-current conversion efficiency (IPCE) measurements were carried out under low-intensity monochromatic light in the wavelength range of 300 – 700 nm using a PTS-2-QE quantum efficiency measurement system (Sciencetech).

3 Results and discussion

3.1 Scanning electron microscope (SEM) images and energy dispersive X-ray spectroscopy (EDS) analysis

SEM and EDS analyses for DSSCs photoanode and CEs are given in the supplementary information file, Figs. S3–S6. Figure S3 shows the SEM and EDS analyses of pure and different concentration of Ho^{3+} , La^{3+} , Er^{3+} and Yb^{3+} doped TiO_2 working electrodes (WEs) synthesized by the sol-gel

method with P25 and applied on the FTO substrate using the ‘Doctor Blade’ technique.

The effect of doping is clearly seen in the SEM images in Fig. S3. There was a change in the morphology of the doped TiO_2 compared to the pure TiO_2 . In this study, TiO_2 (P25-Degussa) powder was used to prepare the paste. P25 has a structure consisting of spherical particle clusters [53, 54]. It has been determined that the morphology of the spherical structures changes with each added element, creating different characteristic structures. The factors affecting the efficiency and film quality of DSSCs include microcracks in the films, clustering of TiO_2 particles in the paste, and weak interfaces between the TiO_2 particles in the coating and the conductive glass. While a certain homogeneity is observed in the pure TiO_2 film without REEs doping, it is observed that the particle size changes after doping and particle clustering occurs in some regions. In Fig. S3, the presence of elements doped to TiO_2 with different percentages (Ho^{+3} , La^{+3} , Er^{+3} , Yb^{+3}) by the sol-gel method is given together with their weight percentages and atomic weight ratios. In the figure, the vertical axis shows the number of detected X-ray counts per second (cps), and the horizontal axis shows the energy (keV). The presence of the doped elements has thus been confirmed and is also supported by XPS. As a result of EDS analysis, it was confirmed that in addition to Ti and O elements, Ho^{3+} , La^{3+} , Yb^{3+} , and Er^{3+} elements were also present in the spectrum and the doping was successful.

By utilizing the SEM analyses shown in Figs. S4, S5, the surface morphologies of the GO-PVP and rGO-PVP structures synthesized by the Hummers method and applied to the CE of DSSCs and applied to the FTO substrate by the ‘Doctor Blade’ technique were investigated.

Examination of the SEM images in Figs. S4, S5 reveals that the GO structures overlap either in a scattered fashion or in multiple layers, which is consistent with the literature. Wrinkles and folds are believed to form as a result of the disruptions of the planar structure of graphene caused by defects and oxygen-containing groups introduced during oxidation. GO nanosheets, composed of randomly stacked and wrinkled thin layers, exhibit clearly visible surface wrinkles and folds. EDS elemental analysis, the presence of elements belonging to PVP as well as C and O elements in the structure proves that this situation creates different structures on the surface. The GO-PVP complex layer exhibits the tightly packed and integrated arrangement of GO flakes; enabling them to spread randomly yet uniformly throughout the volume [55].

The compatibility between GO and PVP polymer is formed by the effect of covalent bonds. The layered and orderly structure of GO, together with its interaction with PVP, results in assemblies in both GO and rGO that are split into multiple monolayers. Asymmetric bonding between functional groups caused only minor folding within the monolayer [56, 57]. rGO exhibits a porous structure characterized by ripples and wrinkles. The presence of ripples is intrinsic to its 2D crystal structure and is essential for maintain the thermodynamic stability of graphene [58].

After the synthesis of GO-PVP and rGO-PVP CE electrodes by the Hummers method, surface elements were identified by EDS analysis and possible impurities in their structures were examined. These analyses are presented in Fig. S6.

The weight and atomic percentages of elements determined by EDS analysis of the GO-PVP and rGO-PVP CE electrodes synthesized by Hummers method are presented in Fig. S6. In addition to C and O from GO and rGO, N from PVP as well as Na and S from SDS ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) used during the GO and rGO synthesis, are also present. While the oxygen content in GO is 17.37%, it decreases to 12.77% in reduced graphene oxide, indicating that the reduction process was effective.

3.2 X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis was conducted to determine the chemical composition and valence states of the elements of pure and TiO_2 doped WEs as well as GO-PVP and rGO-PVP CEs synthesized using the sol-gel and Hummers method.

The general XPS spectrum of pure TiO_2 in Fig. 3a shows that apart from Ti, O, and C no other element peaks are present, indicating the purity of the synthesized WE and absence of contamination. The observation of the C 1s peak may be due to carbon sources in the environment [59]. Ti 2p XPS analysis is presented in Fig. 3b. The binding energies of Ti were determined as 455.80 eV and 461.54 eV for $2p_{3/2}$

and $2p_{1/2}$, respectively, which correspond to the two characteristic peaks of Ti. These results are consistent with the literature, confirm the presence of Ti^{4+} , and validate the pure TiO_2 structure [60]. In Fig. 3c, in the XPS analysis performed to confirm the presence of oxygen in the TiO_2 structure, a peak at 528.0 eV binding energy corresponding to the characteristic O 1s (Ti^{4+}) lattice oxygen (O_L: Ti–O) belonging to the oxygen site was observed [61, 62].

The general XPS spectrum of the 1.0 M La^{+3} TiO_2 photoanode is given in Fig. 4a. It is shown that Ti and O are clearly seen, and La can also be detected for La-TiO_2 nanostructures. The Ti 2p XPS analysis is given in Fig. 4b. It is seen that Ti has two peaks of 455.7 eV and 461.49 eV for the binding energies of Ti $2p_{3/2}$ and $2p_{1/2}$, respectively. In Fig. 4c, the XPS analysis in the oxygen region taken to support the presence of oxygen in the TiO_2 structure shows a peak corresponding to 527.2 eV binding energy, which is the characteristic O1s (Ti^{4+}) lattice oxygen (OL: Ti–O). Figure 4d presents the La^{+3} 3d spectrum in the partial scan region, consistent with Liu et al. [56], showing peaks at 834.09 eV and 847.59 eV for La $3d_{5/2}$ and La $3d_{3/2}$, respectively [63]. It shows that La is doped into TiO_2 in the Ti–O–La bond.

In Fig. 5a, the absence of peaks belonging to elements other than Ti, O, Er and C peaks in the general spectrum of the 0.5, 1.0, and 1.5 M % Er^{+3} doped TiO_2 WE indicates that the synthesized anode does not contain contamination. The C 1s peak can be attributed to environmental carbon [59]. Figure 5b shows the XPS analysis of Ti 2p. The binding energies of Ti for $2p_{3/2}$ and $2p_{1/2}$ were the same for doping ratios of 0.5 M% and 1.0 M%. However, it is seen that there is a slight shift of the binding energy to the right at 1.5 M% doping. In Fig. 5c, in the XPS analysis of the characteristic O1s peak point in the oxygen region taken to support the presence of oxygen in the TiO_2 structure, the doping ratios were the same for 0.5 M% and 1.0 M%. However, it is seen that there is a slight shift of the binding energy to the right at 1.5 M% doping.

XPS graphs of 0.5–1.5 M % Er^{+3} TiO_2 are shown in Fig. 6. According to the literature, the Er $4d_{5/2}$ peak corresponds to 168.0 eV and 166.1 eV binding energy [64, 65]. In another study, the Er^{+3} peak, with binding energies of 167.9 eV and 169.7 eV, was considered to probably indicate the presence of Er_2O_3 and other Er^{+3} species, such as $\text{Er}(\text{OH})_x$ [66]. The Er 4d region was also detected, but curve fitting is challenging due to the complex structure of the Er 4d photoelectron region, with peaks that cannot be fully resolved [67].

In Fig. 7a, the absence of peaks corresponding to elements other than Ti, O, Ho, and C in the general spectrum of the TiO_2 WE doped with 0.5–1.5 M% Ho^{3+} indicates that the synthesized photoanode is free from contamination. In Fig. 7b, Ti 2p XPS analysis is given. The binding energies

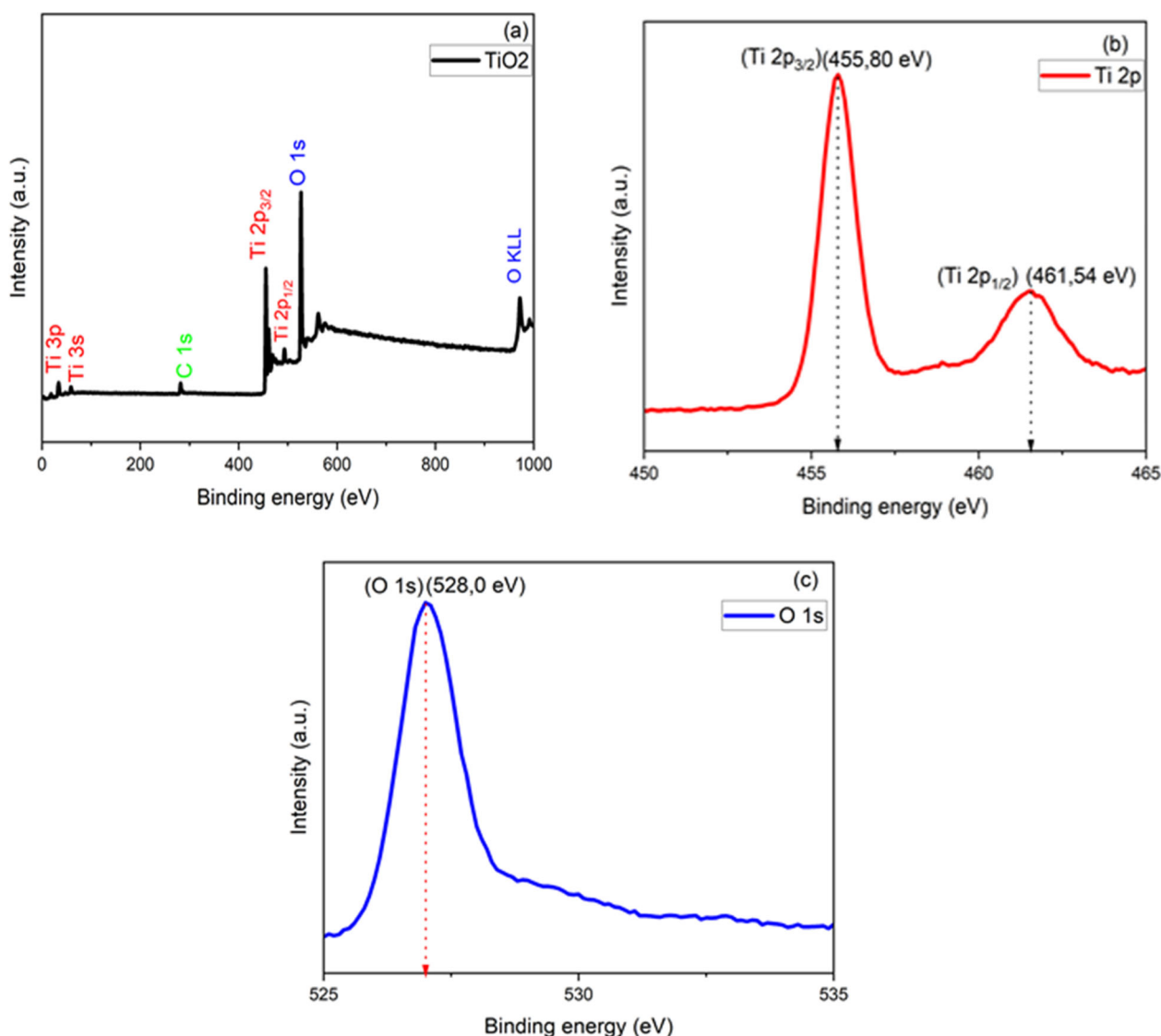


Fig. 3 XPS spectra of pure TiO₂ working electrode **(a)** general spectrum **(b)** Ti 2p **(c)** O 1s regions

of Ti contain very small differences for each doping ratio for 2p_{3/2} and 2p_{1/2}. In Fig. 7c, shows that the characteristic O 1s peak appears at 527.12 eV for all doping ratios, confirming the presence of oxygen in the TiO₂ structure.

In Fig. 8, it is seen that 0.5%, 1.0% and 1.5% M Ho⁺³ TiO₂ photoanodes are similar to the peak corresponding to 163.6 eV binding energy in the literature [68].

The XPS general spectra of 1% M Yb TiO₂ electrode are given in Fig. 9a. Yd 4d peaks at 188.92 eV, Ti 2p peaks at about 456 eV, O 1s peaks at 527.0 eV are confirmed. The peaks at 455.84 eV and 461.61 eV in Fig. 9b are assigned to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, indicating that the main valence of Ti in the obtained sample is +4. The O 1s peak at 527.2 eV in Fig. 9c and the peaks at 188.92 eV for Yb 4d_{5/2} and 196.35 eV for Yb 4d_{3/2} in Fig. 9d prove the presence of Yb³⁺ [69, 70].

XPS analysis of GO-PVP and rGO-PVP used in the CE of DSSCs is presented in Fig. 10. In the general spectrum of

GO-PVP in Fig. 10a, S 2s and Na 1s peaks are observed originating from PVP. Addition, the O 1s peak in rGO showed a decrease intensity after reduction. In Fig. 10b, it is seen that the O 1s peak has a binding energy of 529.62 eV. When the C 1s partial scan is examined in Fig. 10c, it is observed that the binding energies of GO and rGO are quite close to each other [71, 72].

As a result, all these structures given the general XPS spectra of pure and REEs-doped TiO₂ photoanodes in all the figures shown above, indicate that the materials are suitable for photocatalytic or photovoltaic applications.

3.3 Raman analysis

Raman analysis was performed on GO and rGO materials used in the CE of DSSCs. Raman spectroscopy is an effective technique for identifying amorphous and

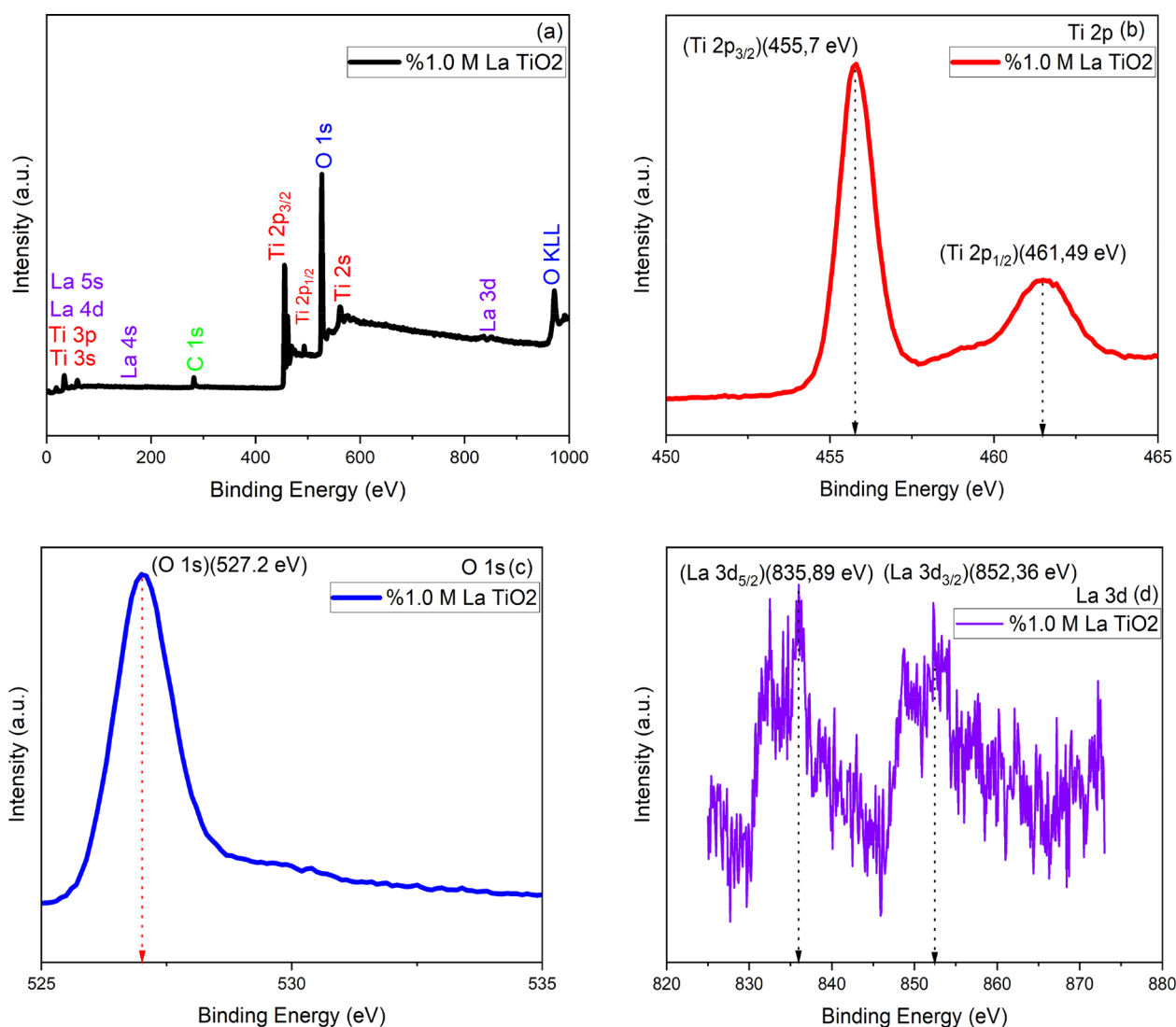


Fig. 4 XPS spectra of the 1.0% La TiO₂ working electrode **a**) general spectrum **b**) Ti 2p **c**) O 1s and **d**) La 3d regions

crystalline regions as well as structural defects and examining electronic properties in carbon nanomaterials [58]. In order to obtain information about the quality and number of layers of GO and rGO, the position, intensity, and ratio of the bands were analyzed in detail. Prior to applying the ‘Doctor Blade’ method on FTO, 1.0% PVP by weight was added to the GO structure synthesized by Hummers method during the synthesis stage. PVP is a widely used polymer due to its chemical stability, excellent optical, mechanical and electrical properties, excellent transparency, easy processing and non-toxic, and due to its solubility in polar solvents, it improves the properties of GO when it forms a nanocomposite compound with GO. PVP is a well-defined synthetic polymer long-chain-linked N-vinylpyrrolidone monomer and can be used as a copolymer in other polymers to form new nanocomposite films [55].

Figure S15 in the supplementary information file shows the Raman spectra of GO-PVP and rGO-PVP used in the CE in DSSCs. Examination of the spectra reveals two characteristic peaks, D and G. These correspond to the D (A_{1g} symmetry, out-of-plane vibration mode, disordered) and G (E_{2g} symmetry, in-plane vibration mode, graphitic) bands. The characteristic Raman peaks of G (graphitic) and D (disorder) are clearly observed in GO and rGO. The D band originating from the breathing mode of j point photons with A_{1g} symmetry, was observed at 1348.30 cm⁻¹ and 1356.40 cm⁻¹ for GO-PVP and rGO-PVP, respectively. In addition, the G band occurring as a result of the first-order scattering of E_{2g} photons by sp² carbon was observed at 1592.02 cm⁻¹ for GO-PVP and 1584.15 cm⁻¹ for rGO-PVP. To evaluate the disorder level in the GO-PVP and rGO-PVP structures, the peak intensities of the D and G bands were proportioned and the I_D/I_G ratio were calculated as 1.03 for

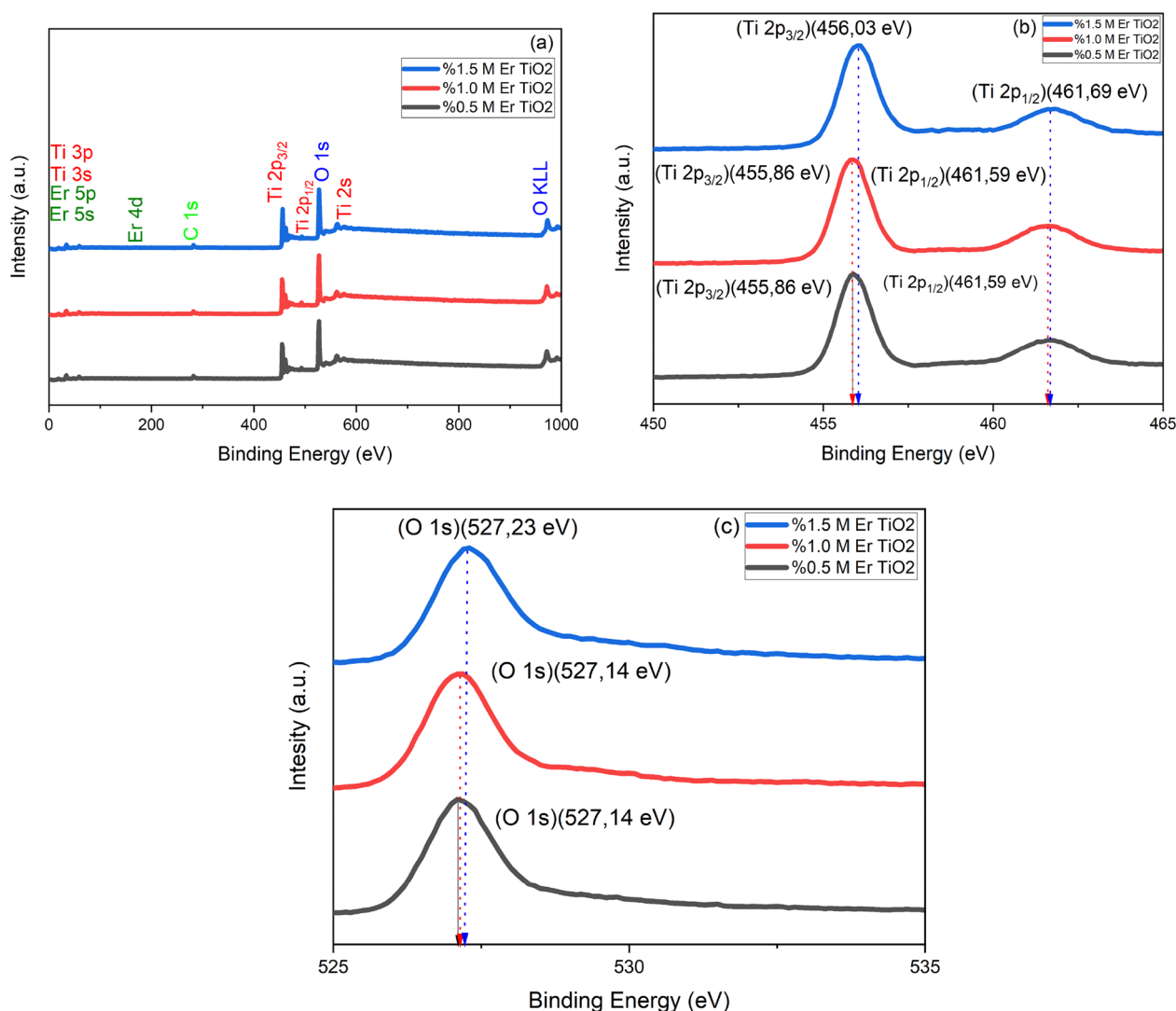


Fig. 5 XPS spectra of 0.5% M, 1.0% M, 1.5% Er³⁺ doped TiO₂ working electrode **(a)** general spectrum **(b)** Ti 2p and **(c)** O 1s regions

GO-PVP and 0.97 for rGO-PVP. The obtained results were found to be consistent with the literature [57, 73]. In the synthesis of graphene oxide, oxygen-containing functional groups were introduced into the graphite layer during the oxidation of graphite, which caused the gap between the layers to increase. Thus, the disordered structure and various defects was formed in the carbon lattice. The intensity of the D peak and the G peak in PVP/GO were similar. This may be due to the interaction of the strong polar amide groups in the PVP polymer chain with the oxygen-containing group in GO. The C O stretching vibration is believed to contribute to the upward broadening of the D peak [56]. The lower ID/IG ratio in rGO-PVP is attributed to the increase in the in-plane sp² conjugated carbon lattice by the addition of PVP nanoparticles. The removal of oxygen groups from GO by the reduction process in rGO caused the graphene to return to its original layer structure.

As a result, the intensity difference of D and G peaks in rGO-PVP to be less than that in GO-PVP [58].

3.4 X-Ray diffraction (XRD) analysis

XRD analysis was carried out to determine the phases, crystal structures and grain sizes of pure and different percentages of REEs (Ho³⁺, La³⁺, Er³⁺, Yb³⁺) doped TiO₂ films produced by the sol-gel method and GO-PVP and rGO-PVP samples synthesized by the Hummers method. The results are presented in the supplementary information file in Figs. S16–S19. In the WE of DSSCs, REEs doping at a rate of 1.0 M% was initially performed and its effect on PCE was evaluated. Subsequently, the percentage values for the element with relatively good results were varied, and their impact on PCE of photovoltaic cells was re-evaluated.

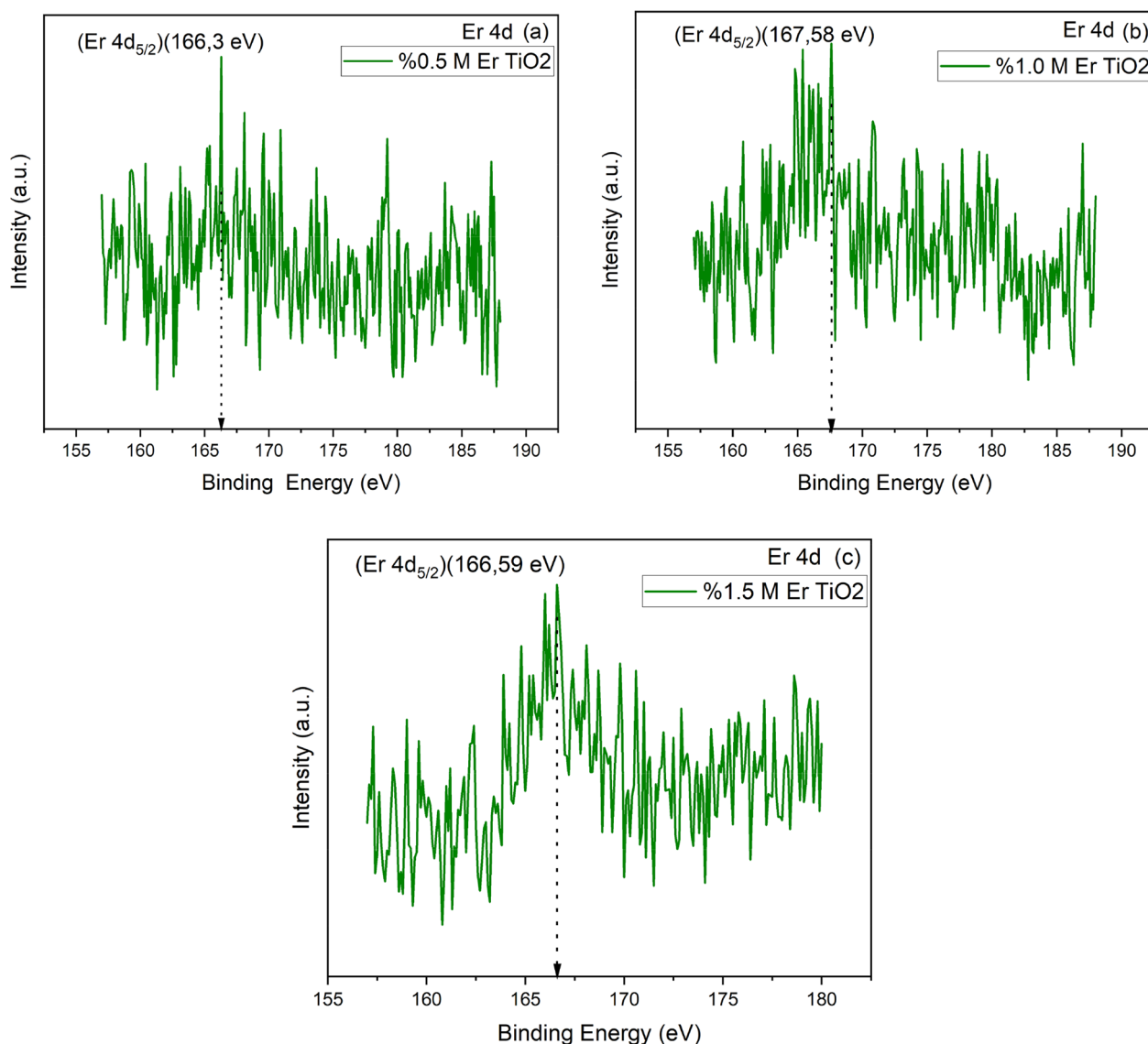


Fig. 6 XPS spectra of Er 4d regions of (a) 0.5 M, b 1.0% M, c 1.5% M Er³⁺ doped TiO₂ working electrode

In the XRD analysis FTO, it was observed that eight distinct peaks of the tetragonal SnO₂ structure were consistent with [JCPDS card No. 041–1445], which are (110), (101), (200), (211), (220), (310), (301) and (321) planes and the intensity values corresponding to these planes were 270, 340, 380, 520, 550, 620, 660 and 790, respectively [74]. TiO₂ synthesized by sol-gel method and TiO₂ samples doped with different amounts of Ho³⁺, La³⁺, Er³⁺, Yb³⁺ were deposited on FTO substrates and thin film XRD analysis was performed. The XRD patterns of pure and doped TiO₂ show that all intensity peaks correspond to (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal planes, respectively, and the intensity values are 250, 380, 480, 540, 550, 630, 690, 700, 750, respectively. This result confirms the formation of anatase phase in doped and pure TiO₂ thin films with tetragonal structure [JCPDS Card No

21-1272] [75]. In TiO₂/FTO XRD diffraction patterns, the presence of a weak intensity peak corresponding to FTO is also observed. In the XRD pattern of doped TiO₂ thin films, there are characteristic diffraction peaks belonging to the anatase phase, similar to the XRD pattern of pure TiO₂ [76, 77]. As the doping ratio increases to 1.5%, a slight decrease and broadening of the peak intensities are observed. The incorporation of doping ions to the crystal lattice of TiO₂ creates stress in the system, leading to a reduction in the crystal symmetry. The results obtained from XRD analysis and the observed peaks are consistent with the data reported in the literature. It also shows that pure and doped TiO₂ thin films were successfully deposited onto FTO and that no other impurities or contaminants are present. GO synthesized by Hummers method and rGO subjected to reduction process afterwards, PVP was added

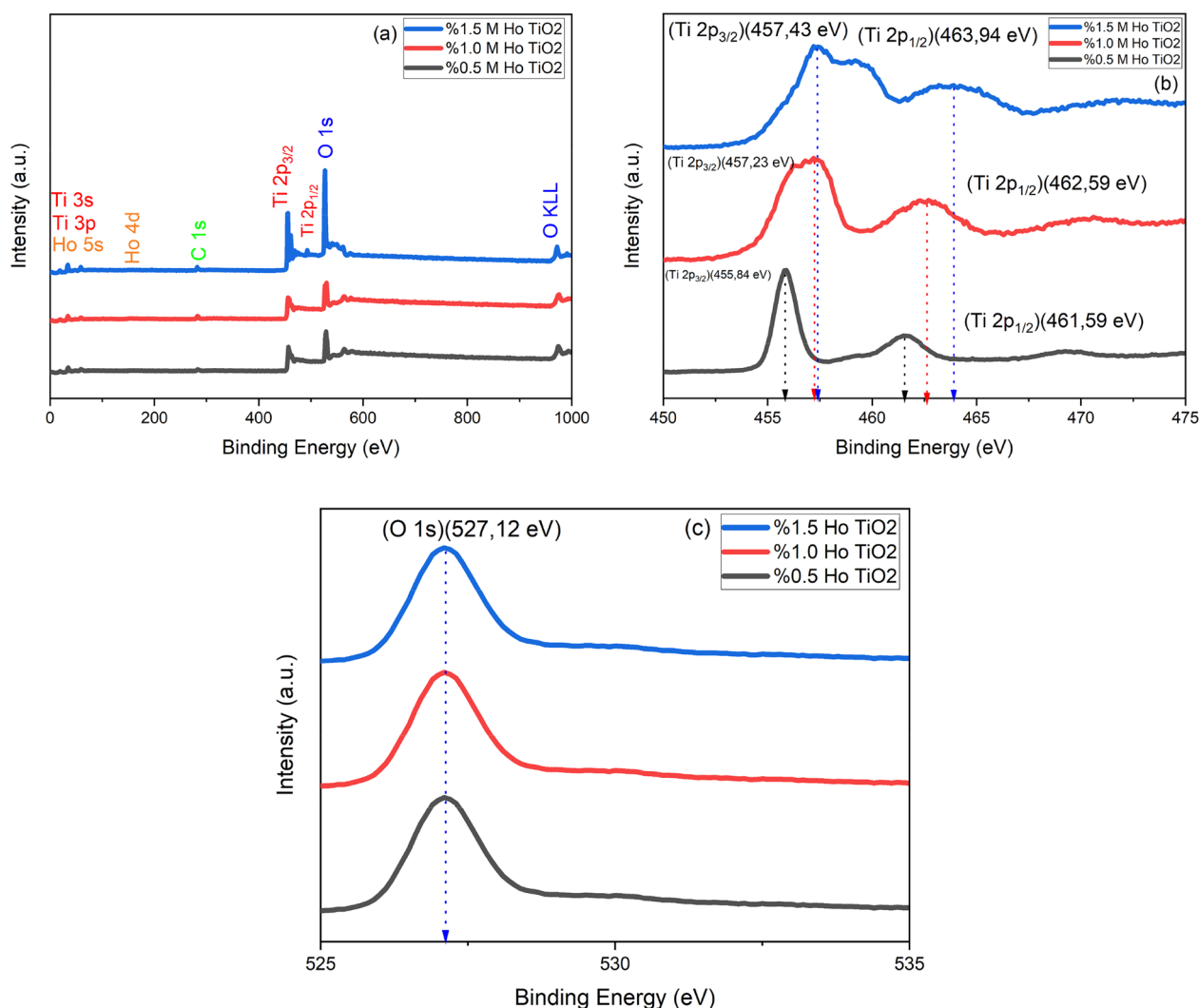


Fig. 7 XPS spectra of the TiO₂ working electrode doped with 0.5% M, 1.0% M, 1.5% Ho³⁺ (a) general spectrum (b) Ti 2p and (c) O 1s regions

to FTO base material before the ‘Doctor Blade’ method was applied in order to create nanocomposite CE and XRD patterns of these samples are presented in Fig. S20. GO exhibits two diffraction peaks: One a prominent peak at 11°, correspond to the (001) plane, which appears weak peak due to the influence of PVP. The other peak is observed very weakly at (2θ) 43° and this peak corresponds to the (002) plane. The PVP-GO peak is observed at 27° (2θ) [73]. rGO-PVP shows a single diffraction peak at 23°, representing rGO-PVP [57, 78].

The crystal sizes (D) of pure TiO₂ and REEs-doped TiO₂ structures, synthesized by the sol-gel method and applied onto FTO using the ‘Doctor Blade’ method, were calculated using the Debye-Scherrer formula shown below.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

In this formula, k represents the particle shape factor (0.9 for spherical particles), β represents the full width at half maximum (FWHM) of the diffraction peak of the selected crystal. λ represents the wavelength of the X-ray source (0.15406 nm), and θ represents the Bragg angle at 2θ, which corresponds to the maximum peak intensity of the diffraction peak. The crystal sizes were calculated by substituting the measured values into the equation using the Origin program, and the results are presented in Table S2 of the supplementary information. As a result of the calculations, showed that the doping decreased the crystal size in D values and caused an increase in the FWHM value. In addition, a slight shift in the 2θ values was observed. The decrease in the crystal size provides a larger specific surface area, enhancing the adsorption of dye molecules.

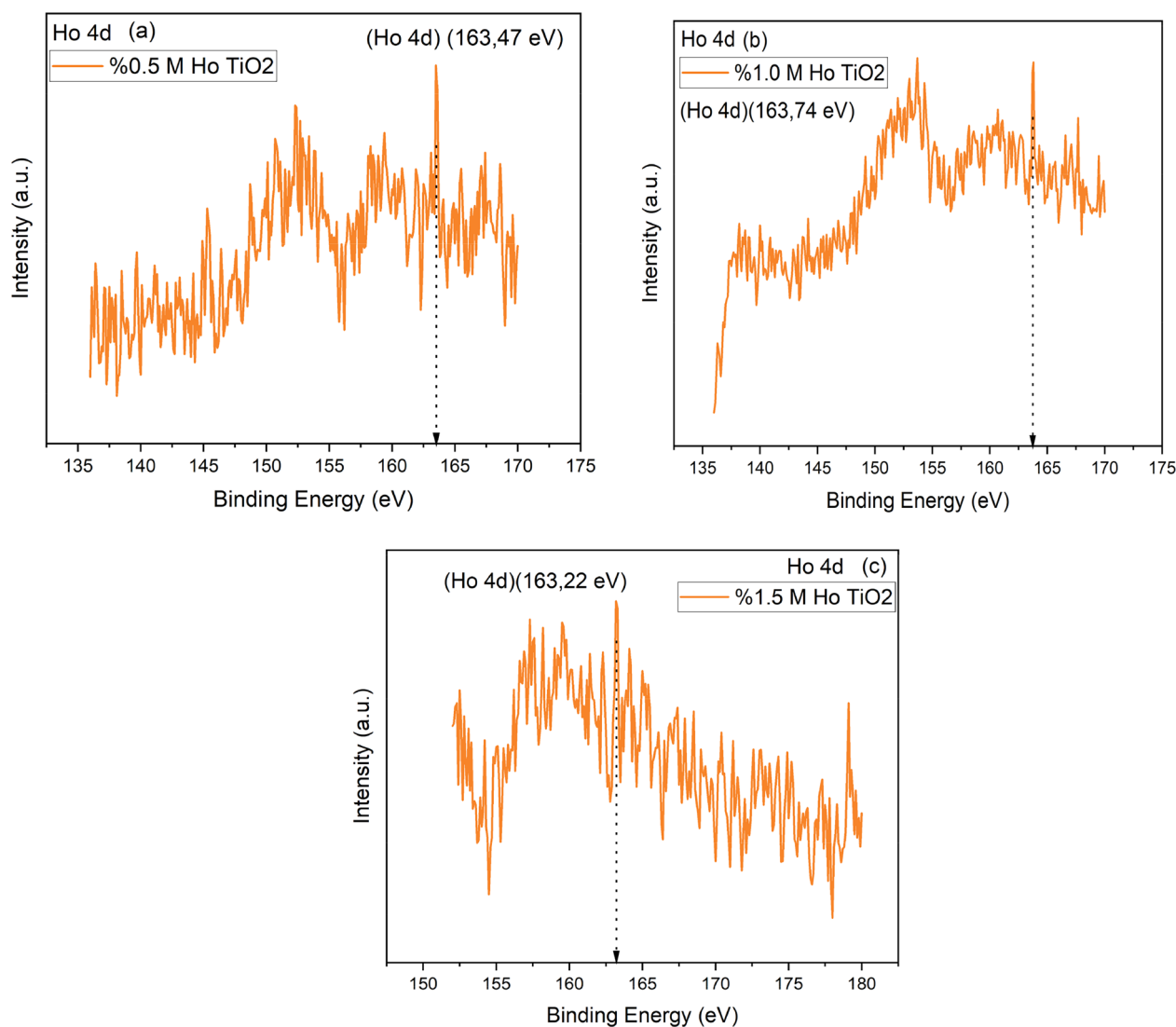


Fig. 8 XPS spectra of Ho 4d regions of TiO₂ working electrode doped with (a) 0.5% M, b 1.0% M, c 1.5% M Ho³⁺

3.5 Brunauer-Emmett-Teller (BET) analysis

In DSSCs, the dye adsorption occurs on the surface of the semiconductor, and the amount of adsorbed dye depends on the surface area of the semiconductor or composite material [79]. In general, the good PCE properties (short-circuit current density (J_{SC}), and photocurrent efficiency (η)) of DSSCs are due to the optimum porosity of the photoanode TiO₂ film, which enables the effective distribution of dye and electrolyte. Furthermore, the high specific surface area of TiO₂ particles promotes efficient adsorption substrate of the light-harvesting sensitizer [80]. The BET surface area and pore size distribution of pure TiO₂ and 1.0% M Ho³⁺, La³⁺, Er³⁺, Yb³⁺ doped TiO₂ used in the WE of DSSCs were investigated using N₂ adsorption-desorption isotherms. BET analysis was performed to evaluate the effect

of doping the surface area and pore size, and the results are presented in Figs. 11–15.

The graphs were generated by Barrett–Joyner–Halenda (BJH) method to determine the pore size distribution. Among the six different types of nitrogen adsorption/desorption isotherms, were found to be the isotherms of photoanodes were consistent with Type-IV isotherm and these isotherms had type H₂ hysteresis loops. This type of isotherm indicates the presence of mesopores in the structure. The mesoporous structure provides a suitable medium that facilitates the diffusion and conduction of the electrolyte during electrochemical reactions [81].

TiO₂ nanostructures with a large surface area and narrow pore size distribution, when used as photoanodes in DSSCs, provide higher dye loading and more efficient electrolyte transport. These properties contribute to improve of charge

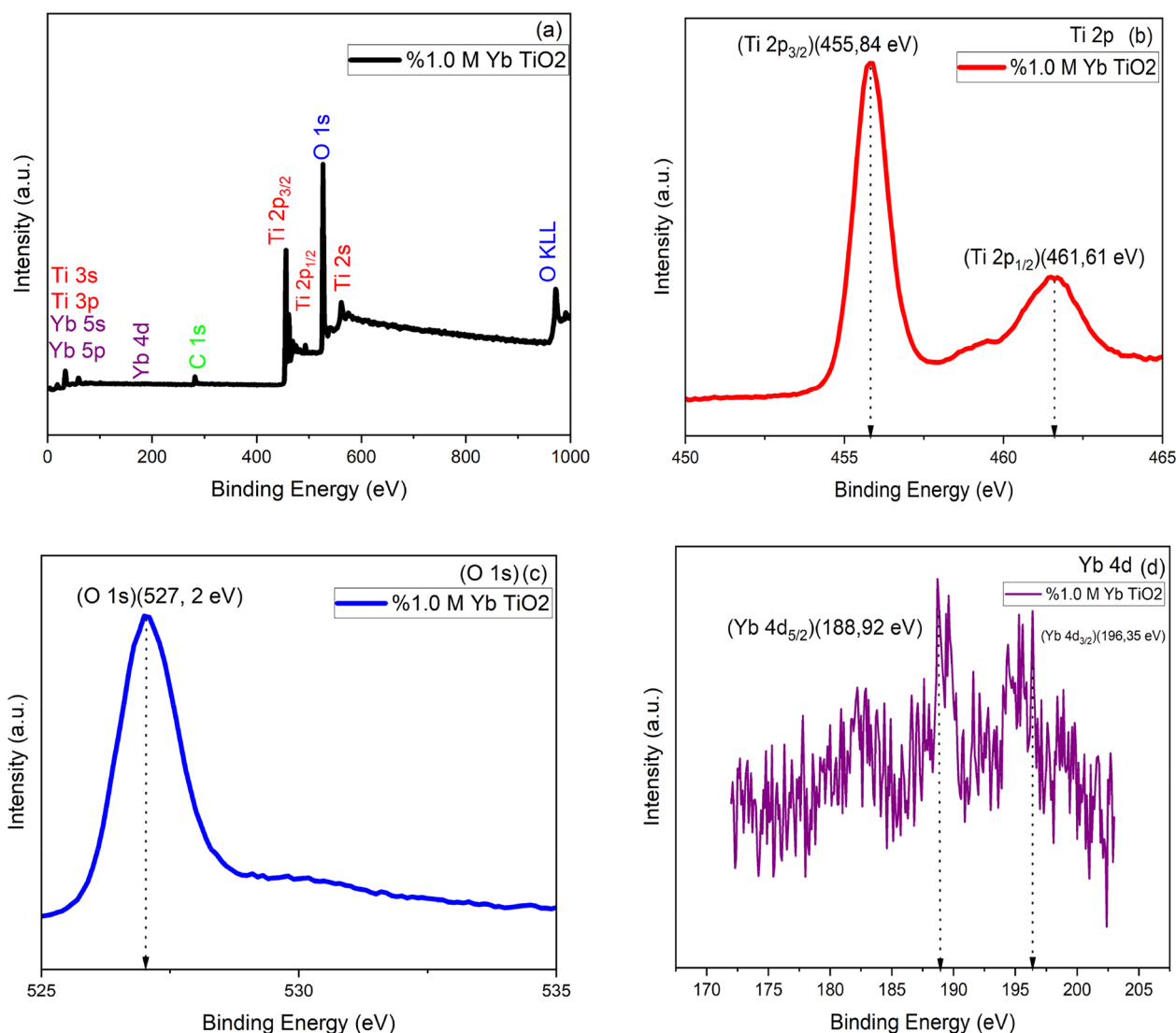


Fig. 9 XPS spectra of the 1.0% Yb TiO₂ photoanode **(a)** general spectrum **(b)** Ti 2p **(c)** O 1s and **(d)** Yb 4d regions

transport, which are two important factors in increasing the PCE of DSSCs [79]. The high surface area provides more sites for dye adsorption, enhancing photogenerated electron transfer through the fast photoelectron transfer channel, thereby facilitating circuit completion [82]. This indicates that when the specific surface area of TiO₂ increases with doping, the uniform dispersion of dopants on the TiO₂ surface promotes the formation of photocatalytic and adsorption active sites.

The specific surface area of TiO₂ increases with doping, indicating that the dispersion of dopants on the TiO₂ surface, photocatalytic, and adsorption active sites are enhanced. Therefore, TiO₂ doping is expected to enhance dye uptake and light absorption in DSSCs for some elements, thus increasing the photo efficiency. In the PCE (I-V) analysis of DSSCs, it was observed that doping certain elements into pure TiO₂ has a positive effect on the PCE,

whereas other elements negatively affect it. Table S2 presents a numerical evaluation of the structural properties of the WEs and their impact on DSSCs performance. The surface areas of the photoanodes vary with the addition of 1.0 M REEs. According to Table 2, it is observed that the 1.0 Ho TiO₂-N-rGO coded cell has the highest surface area, current density, and conversion efficiency.

The effect of the surface area and size of TiO₂ particles on the charge transport properties has been confirmed in previous studies. In this context, electron transport through the TiO₂ network has a direct effect on the mean free path length of the particle size. Larger particle sizes allow longer transport distances and reduce collision probabilities. Additionally, the surface area significantly affects the recombination rate when interacting with the electrolyte. In this case, large TiO₂ particles with high recombination resistance, low transport resistance, and low chemical

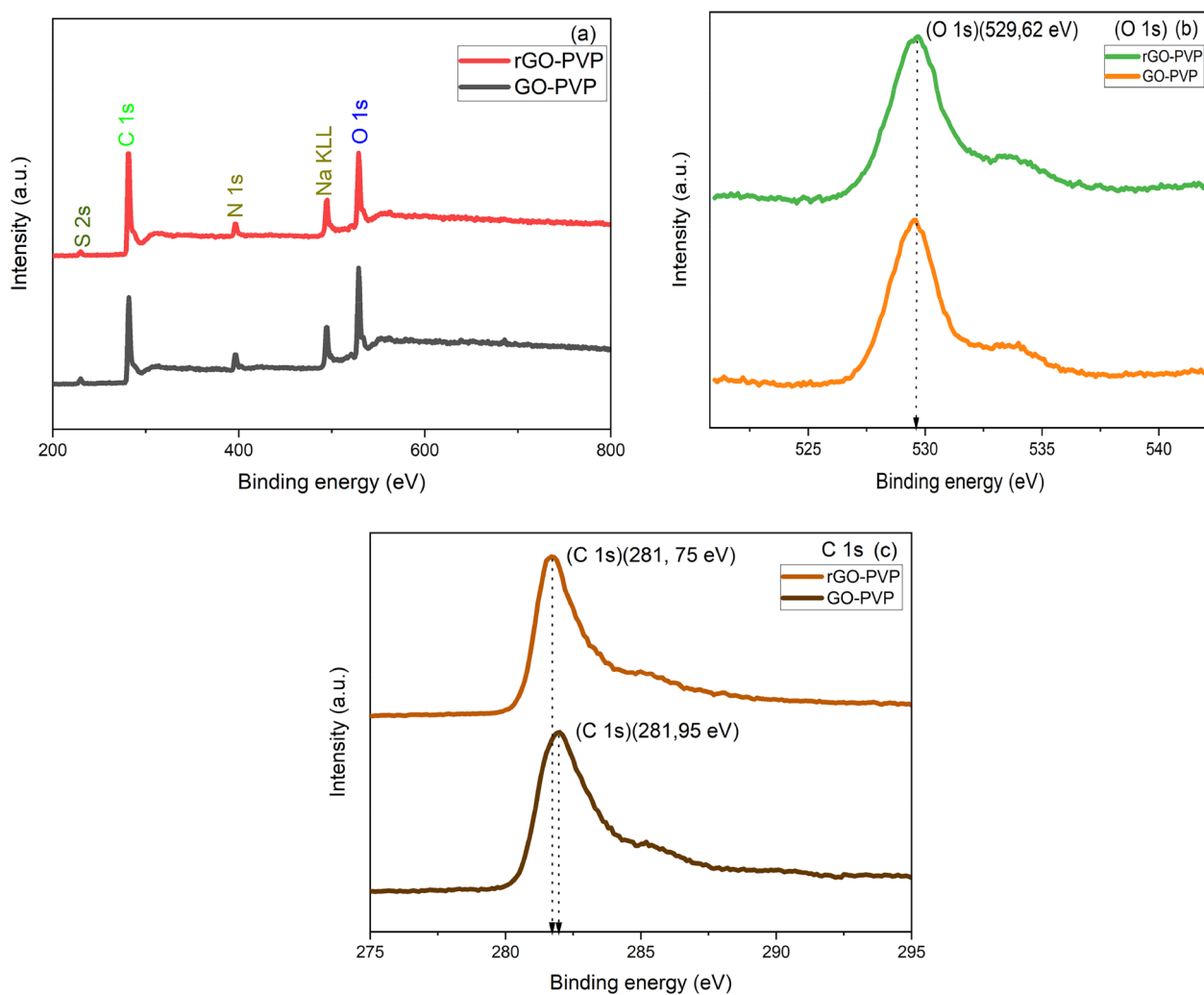


Fig. 10 XPS spectra of GO-PVP and rGO-PVP counter electrodes **(a)** general spectrum **(b)** O 1s and **(c)** C 1s regions

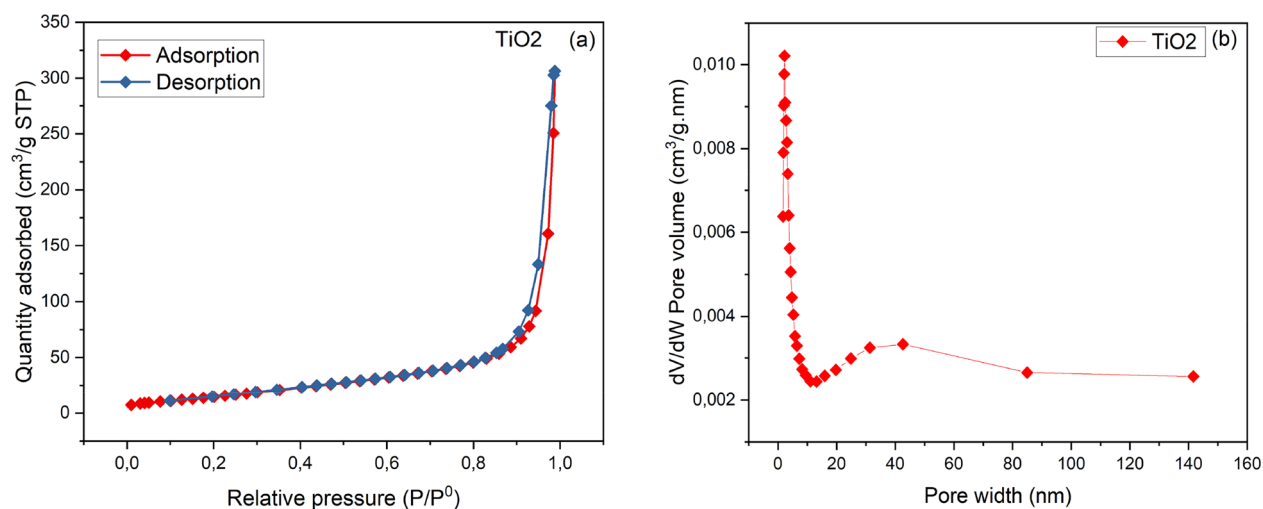


Fig. 11 Pure TiO₂ **(a)** N₂ adsorption-desorption isotherms **(b)** BJH pore size distribution

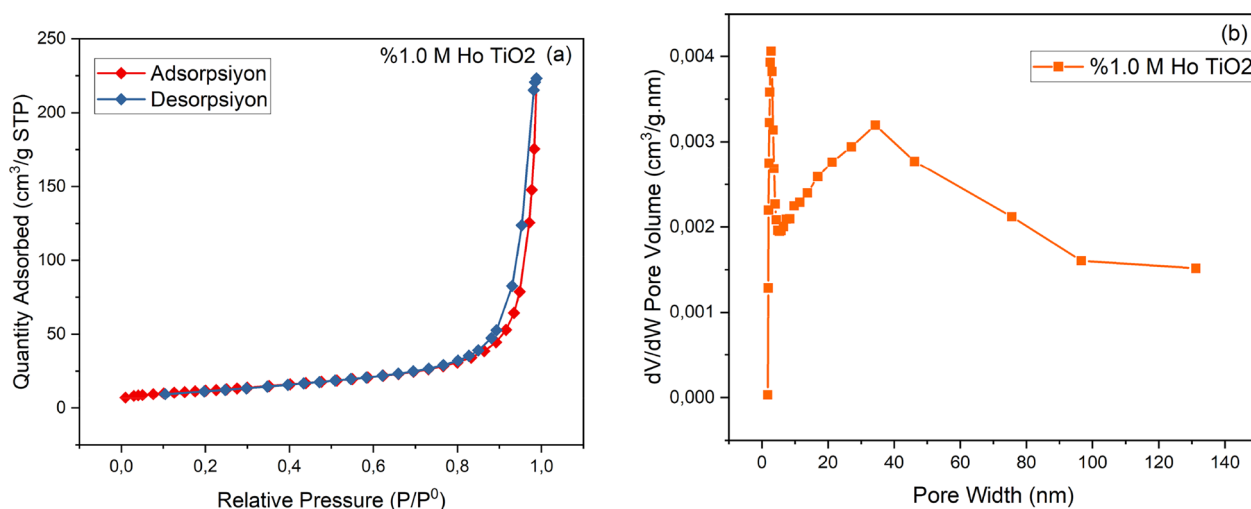


Fig. 12 1.0% M Ho³⁺ TiO₂ (a) N₂ adsorption-desorption isotherms **b** BJH pore size distribution

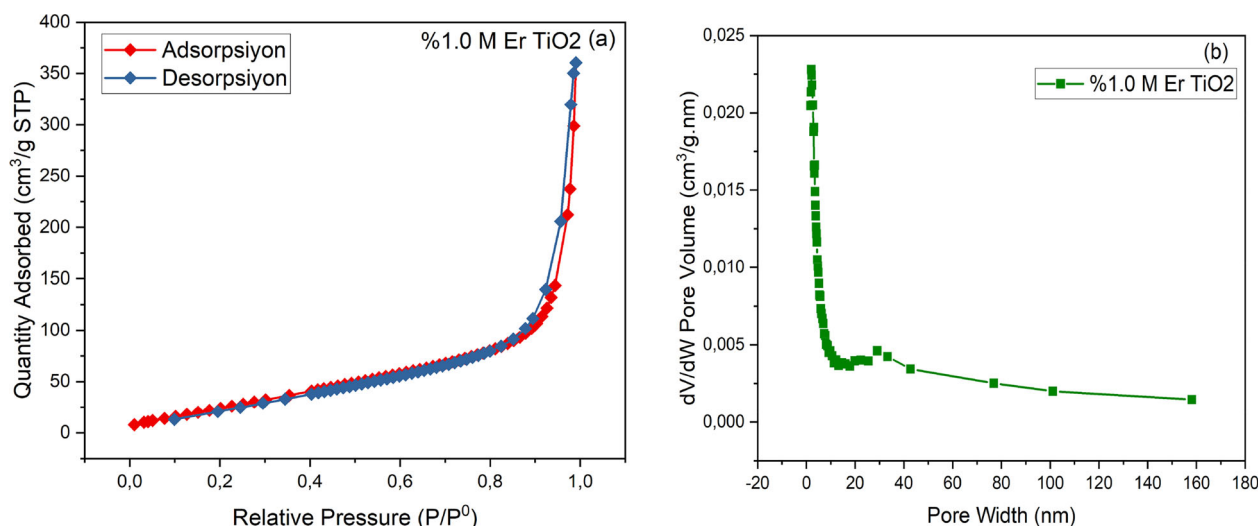


Fig. 13 1.0% M Er³⁺ TiO₂ (a) N₂ adsorption-desorption isotherms **b** BJH pore size distribution

capacitance are expected to have longer diffusion paths and thus higher efficiency. In the WE where TiO₂ nanoparticles are used, a balance should be established between the morphological factors of TiO₂, which determine the light harvesting capacity of the entire network, and the charge collection efficiency, which is affected by the particle size [83].

3.6 UV-visible spectrophotometer measurements and optical analysis

In order to determine the optical properties in the ultraviolet (UV) and visible regions, absorption measurements of pure TiO₂ and REEs doped TiO₂ thin films synthesized by sol-gel method in the range of 300–700 nm were evaluated. Furthermore, the change in the band gaps with doping to

TiO₂ was determined using the $(\alpha h\nu)^2$ - Band Gap (Photon energy-eV) graph. Using the Tauc equation, the band gap (E_g) of pure and doped TiO₂ thin films was calculated, and the results are given in supplementary information file in Figs. S26–S30.

The graphs clearly demonstrate that the doping process alters the absorption properties of the material. Spectral analyses indicate that pure and doped TiO₂ exhibit strong absorption in the UV region, while showing weaker absorption in the visible region. Crystal defects induced by the dopant lead to variations in the energy range of the materials. Moreover, the energy range is affected by many parameters such as particle size, impurity centers, micro-strain, light absorption, oxygen vacancies, substitution density, and film thickness. The band gap values of the photoanodes presented in supplementary information file in

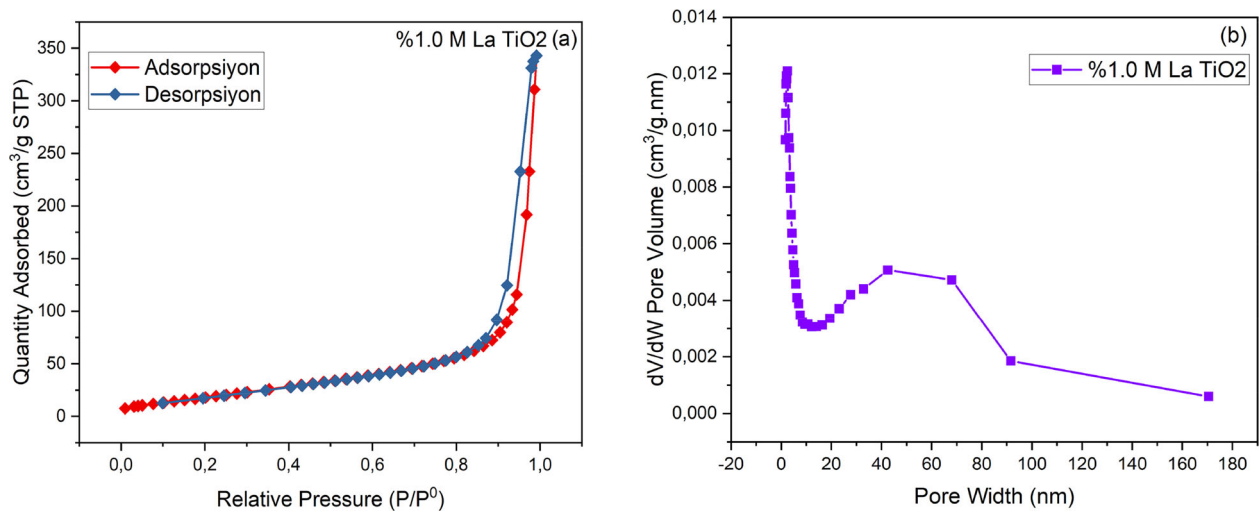


Fig. 14 1.0% M La⁺³ TiO₂ (a) N₂ adsorption-desorption isotherms (b) BJH pore size distribution

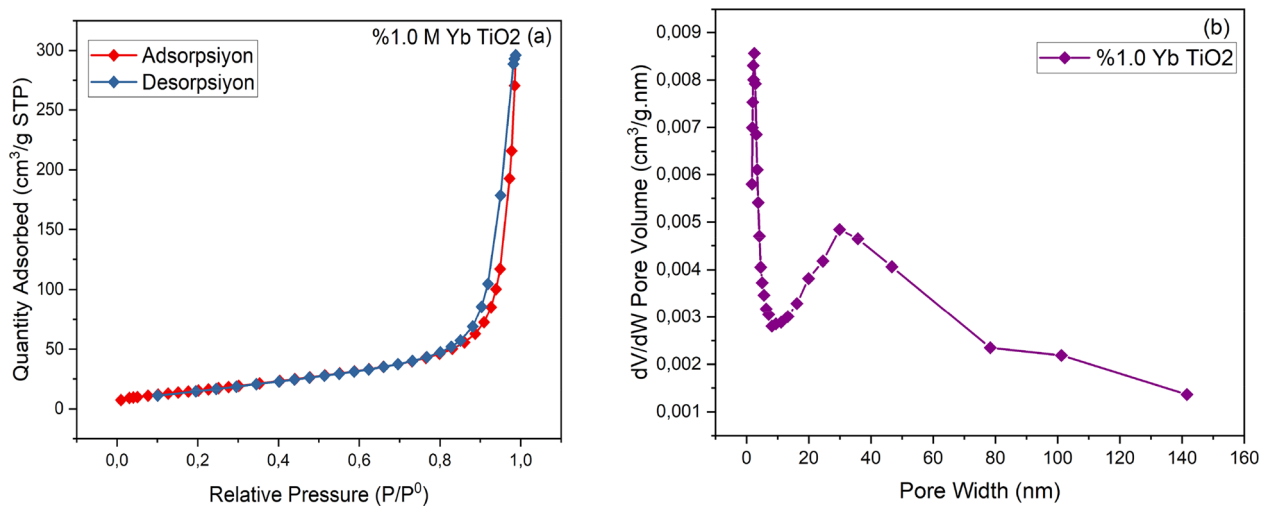


Fig. 15 1.0% M Yb⁺² TiO₂ (a) N₂ adsorption-desorption isotherms (b) BJH pore size distribution

Table 2 Structural properties of pure TiO₂ and 1.0% M (Ho⁺³, La⁺³, Er⁺³, Yb⁺²) doped TiO₂ working electrodes based on BET analysis

Working Electrode	BET Surface Area (m ² /g)	Average Particle Size (nm)	Adsorption Pore Volume (BJH) (cm ³ /g)	Desorption Pore Volume (BJH) (cm ³ /g)	Adsorption Pore Size (BJH) (nm)	Desorption Pore Size (BJH) (nm)
TiO ₂	58,54	102,5	0,447	0,448	23,88	22,84
%1,0 M Ho TiO ₂	111,07	166,32	0,550	0,558	16,37	15,66
%1,0 M Er TiO ₂	60,61	98,98	0,457	0,456	24,08	22,49
%1,0 M La TiO ₂	59,78	100,37	0,412	0,412	22,41	21,90
%1,0 M Yb TiO ₂	38,85	154,45	0,344	0,344	30,06	27,40

Table S4 reveal that the increase in the doping amount causes a decrease in E_g values. This decrease in E_g enhances the optical properties by allowing the material to absorb more photons and enabling the participation of low-energy photons in the photoreaction process. Nanoscale size changes directly affect in optical properties. The quantum confinement effect observed at small sizes generates new sublevels in the energy levels of the films and leads to separation in the band structure. Consequently, different sizes to exhibit different band gap values [84, 85].

Table 3 Performance results of DSSC of TiO_2 thin films with properties given in Table 1

Cell Code	V_{OC} (V)	J_{SC} (mA/cm^2)	P_{MAX}	FF	PCE (η) (%)
$\text{TiO}_2\text{-N-GO}$	0,71	6,06	0,17	0,39	0,85
$\text{TiO}_2\text{-H-GO}$	0,57	0,57	0,03	0,76	0,13
$\text{TiO}_2\text{-N-rGO}$	0,69	8,39	0,3	0,51	1,5
$\text{TiO}_2\text{-H-rGO}$	0,56	0,95	0,03	0,55	0,15

Spectrophotometric analyses of N-719 and hibiscus plant sensitizers in liquid form were performed. Optical absorption spectra of the samples were recorded and the results are shown in Fig. S31a, b.

As shown in supplementary information file in Fig. S31a, the absorbance spectrum of N-719 dye exhibits strong absorption in a wider spectral range of 300–400 nm and 500–600 nm compared to hibiscus dye covering the visible and near UV regions. These findings are consistent with the data reported in the literature [86–89]. As shown in supplementary information file in Fig. S31b, the absorbance spectrum of the hibiscus dye containing anthocyanin pigment exhibits a distinct peak in the visible region at approximately 520 nm in the wavelength range of 500–600 nm. This wavelength range is consistent with previously reported literature values [36, 39–41]. Since the wavelength width of N-719 dye is wider compared to hibiscus dye with anthocyanin pigment, it increases the utilization of incident light,

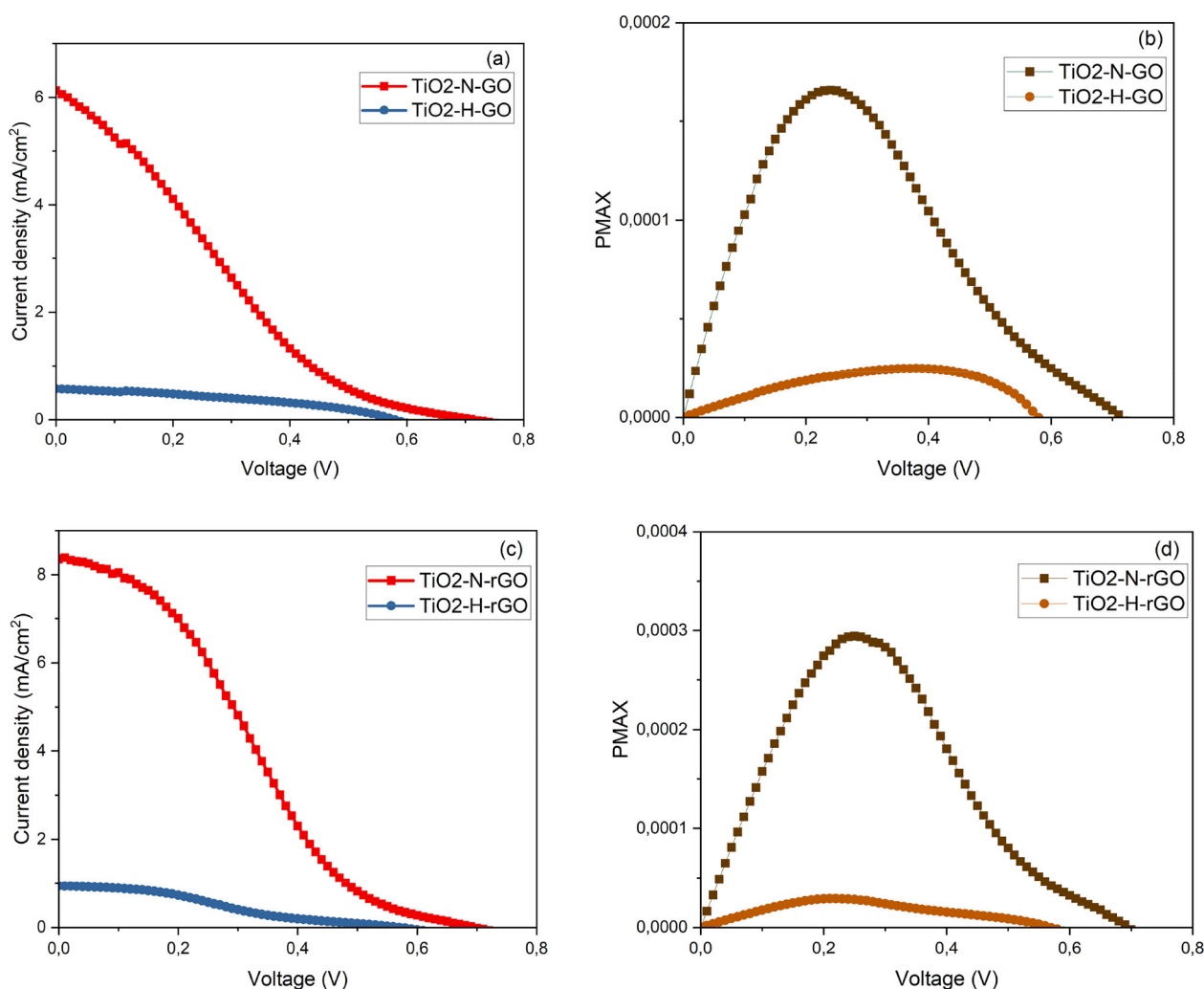


Fig. 16 J-V graph of (a) GO at the cathode c rGO at the cathode DSSCs, b GO at the cathode d rGO DSSCs, whose properties are given in Table 1

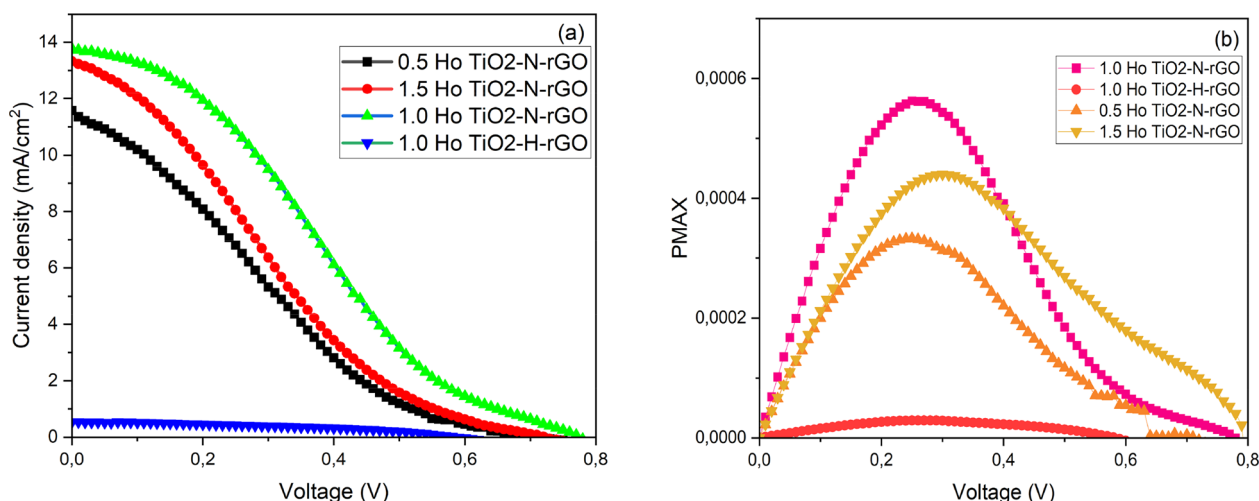


Fig. 17 P_{MAX} -V graphs of DSSCs (a) and b of TiO₂ thin films doped with 0.5%, 1.0% and 1.5% M Ho⁺

which improves the PCE by enhanced photocurrent generation.

3.7 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR spectroscopy was employed to analyze the bond structure of N-719 and sensitizers obtained from hibiscus plant in liquid form. FTIR spectrum of N-719 and hibiscus dyes obtained from hibiscus plant is given in supplementary information file in Fig. S32a.

In the FTIR spectra obtained with variable wavelengths representing various functional bonds in Fig. S32a, the transmittance peak in N-719 dye is located at 3399 cm⁻¹ wavelength and indicates the N-H functional group. Additionally, the presence of the band at 2971 cm⁻¹ corresponds to the stretching of the C-H bond. The COO⁻ symmetric stretching is observed at approximately 1365 cm⁻¹ [90]. The presence of C=O and -OH groups is revealed by distinct peaks in the regions of 1600–1750 cm⁻¹ and 3000–3250 cm⁻¹, respectively. Furthermore, a peak at approximately 1072 cm⁻¹ due to C-O group vibrations is observed [91–93].

Natural dyes are expected to contain active functional groups for effective adsorption onto the photoelectrode thin film. FTIR analysis of hibiscus dye containing anthocyanin pigment at wavenumbers between 4000 and 500 cm⁻¹ is shown in supplementary information file in Fig. S32b. The graph clearly shows that hydroxyl (-OH) groups are present at approximately 3300 cm⁻¹ and carbonyl (-CO) groups are present at 1049 cm⁻¹ [94]. The peak at 881 cm⁻¹ is due to C-O-C aliphatic ester stretching, whereas the peaks at 1362 cm⁻¹ and 2961 cm⁻¹ occur due to the effect of C-H in-plane bending vibrations [37, 95]. In DSSCs, OH and

C=O functional groups stand out because these groups play an important role by binding to the photoanode material to enable the transition of electrons from the HOMO to the LUMO of the dye to the conduction band of the photoanode material [94]. Since both N-719 and the sensitizers prepared by extracting from the hibiscus plant were prepared in ethanol solvent, their spectra exhibit similar features.

3.8 Calculation of photovoltaic parameters of DSSCs using pure and REEs doped TiO₂ thin film in WE (I-V measurements)

I-V measurements of DSSCs were carried out using a Keithley 2400 device, voltage was applied and current values were recorded at certain intervals. These measurements were conducted using the HelioSim CL60 solar simulator under 100 mW/cm² illumination with a filter in the AM 1.5 G standard and at room temperature. Current density (J)-Voltage (V) curves of DSSCs are given in Figs. 16–20. Additionally, the performance results of DSSCs are summarized in Tables 3 and 4.

To investigate the effect of TiCl₄ in cells with PCE above 1.0%, 0.05 M TiCl₄ was deposited onto the cleaned FTO base material, and after waiting for 50 min at 70 °C, the pastes prepared with the sol-gel method were applied with the ‘Doctor Blade’ technique and calcined at 500 °C for 1 h. The graphs of DSSCs treated with TiCl₄ are shown in Fig. 21, and the performance results are presented in Table 5.

The P_{max}-V curves of the DSSCs using Pt in the CE is shown in Fig. 22 and the performance metrics are shown in Table 6. The findings in Table 3 show that the use of rGO instead of GO in the CE increases the PCE by increasing the current density (J_{SC}). However, the efficiency of the

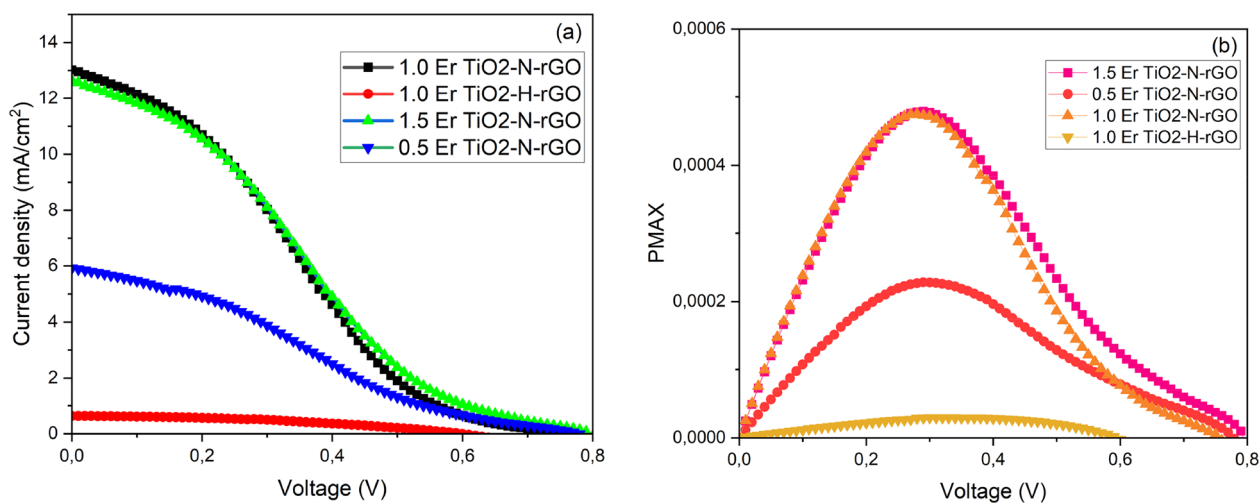


Fig. 18 P_{MAX} -V graphs of DSSCs (a) and b of TiO_2 thin films doped with 0.5%, 1.0% and 1.5% $M Er^{+3}$

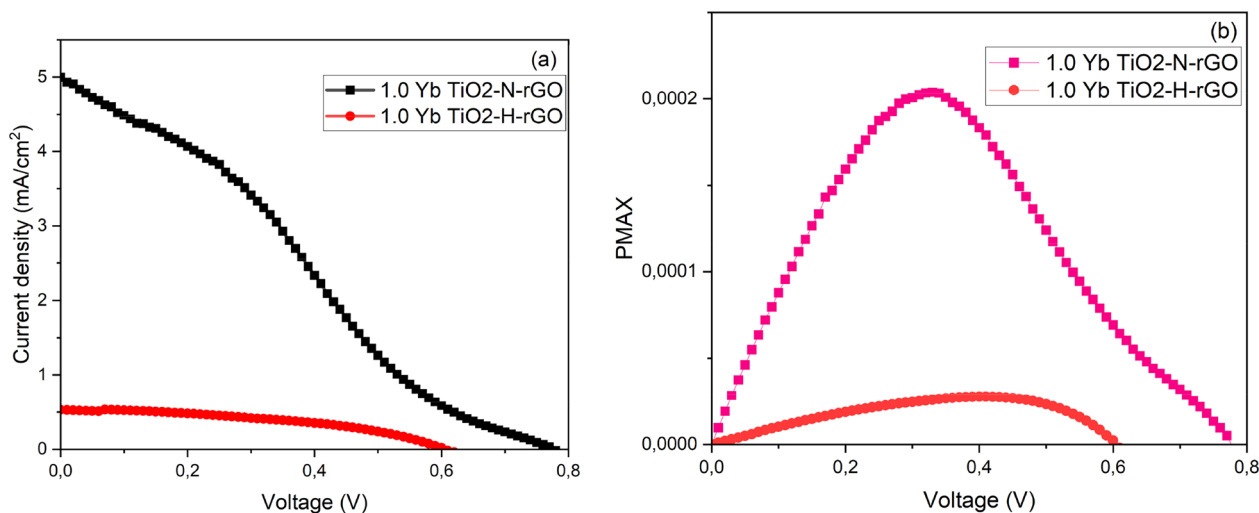


Fig. 19 P_{MAX} -V graphs of DSSCs (a) and b of TiO_2 thin films doped with 0.5%, 1.0% and 1.5% $M Yb^{+2}$

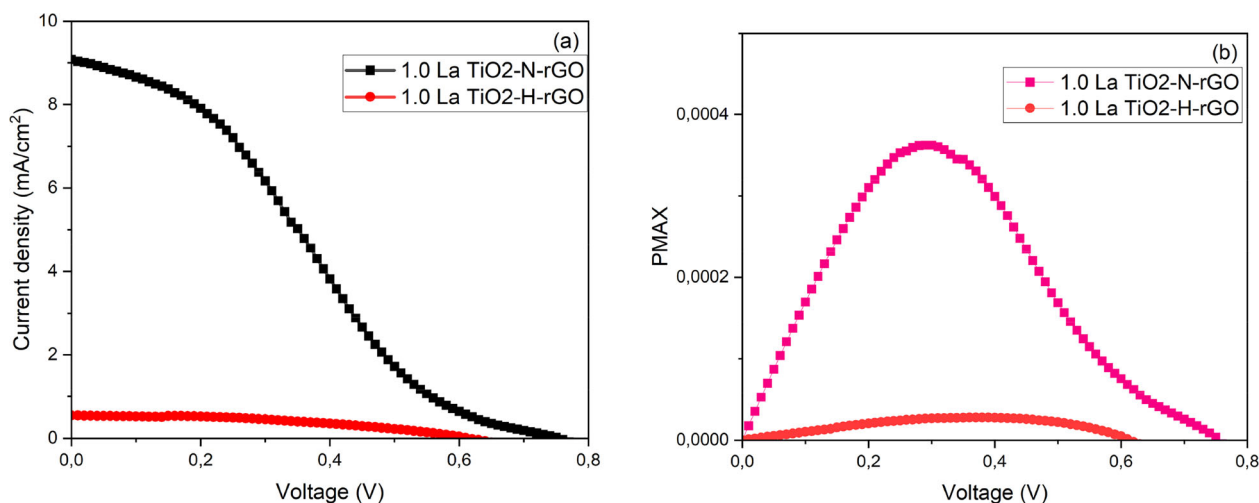


Fig. 20 P_{MAX} -V graphs of DSSCs (a) and b of TiO_2 thin films doped with 0.5%, 1.0% and 1.5% $M La^{+3}$

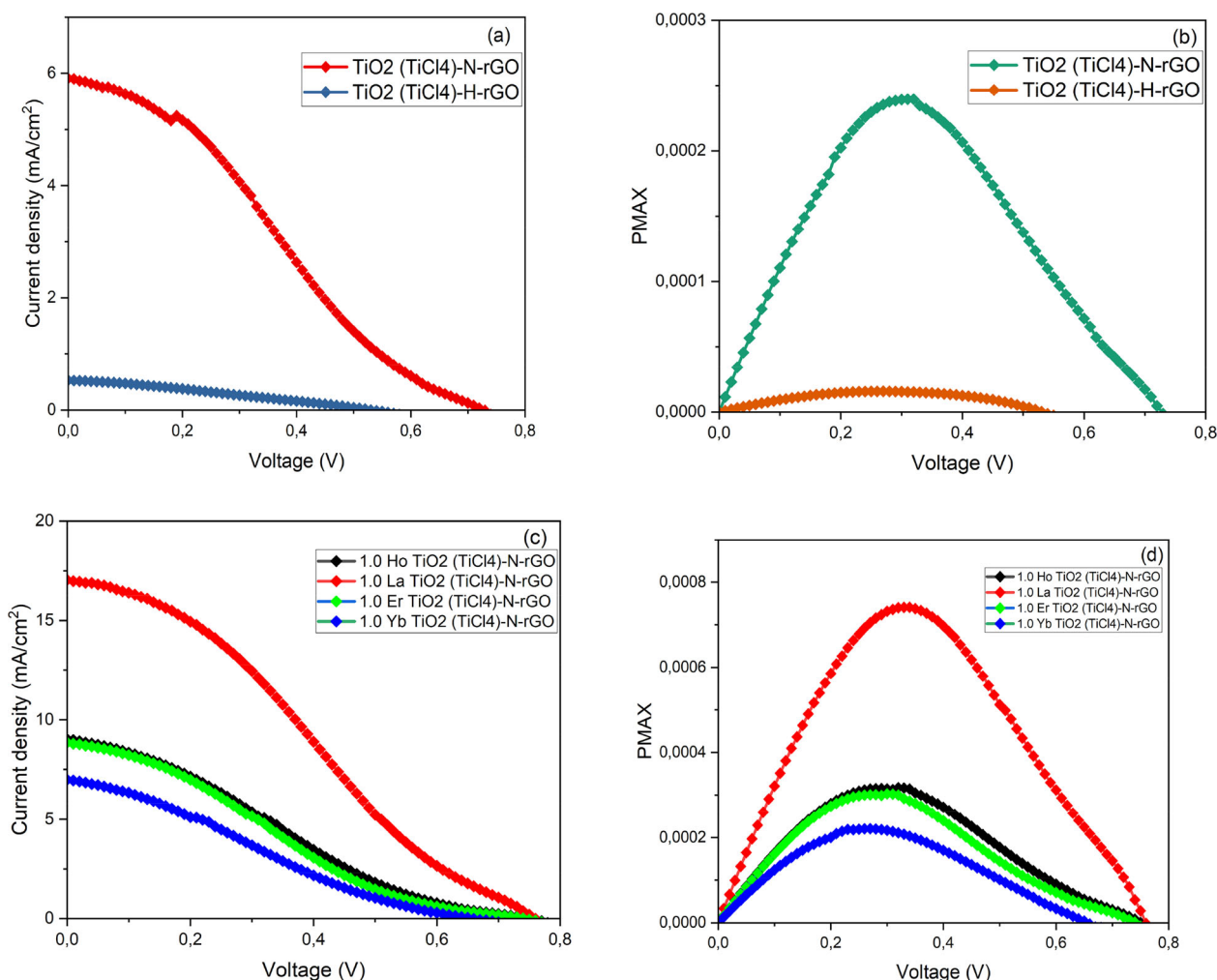


Fig. 21 a, c J-V and b, d graph of DSSC treated with TiCl_4

Hibiscus plant remained below the efficiency provided by N-719. In the cells where GO was used as the CE, the efficiency was lower compared to rGO. For this reason, rGO was selected as the CE material in the fabricated cells. The efficiency of the $\text{TiO}_2\text{-N-rGO}$ cell, which was 0.85%, increased to 1.5% in the $\text{TiO}_2\text{-N-rGO}$ cell and was found to be 76% higher. The main reason for this is that while GO has semiconductor properties close to insulators, rGO has a much higher conductivity. Furthermore, the specific surface area of rGO is larger compared to GO.

The practical applications of TiO_2 nanoparticles as photoanodes are limited due to the high electron-hole pair recombination rate and low quantum efficiency resulting from low electron transport. An effective approach to overcome these problems would be to apply the doping procedure that allows the electron-hole clusters to be effectively isolated by shaping the crystal deformities or vacancy states in the material/matrix and thus to increase the quantum efficiency and electron transport. Among the lanthanide element doped DSSCs, 1.0 Ho $\text{TiO}_2\text{-N-rGO}$ cell

exhibited the best performance with 2.87% efficiency. While the efficiency of $\text{TiO}_2\text{-N-rGO}$ cell was 1.5%, 1.0 Ho $\text{TiO}_2\text{-N-rGO}$ cell provided 91% increase with 2.87% efficiency. REEs have the properties such as having 4 f electron configuration that reduces the recombination of electron-hole recombination and can promote the chemical adsorption of organic molecules on TiO_2 crystal surfaces, thus improving the light harvesting ability [96]. It is proposed that REEs doping, by virtue of the unique photoluminescence properties they impart to DSSCs, expands the spectral light absorption range of the cells via UC and DC mechanisms and improves device performance.

For REEs, increasing the Ho^{3+} doping ratio from 1.0% to 1.5% resulted in a decrease in efficiency, whereas a slight increase was observed for Er^{3+} . This is due to the slight increase in the V_{OC} value in Er^{3+} . In all cells doped with metal and lanthanide elements, the efficiency of the cells sensitized with the dye obtained from the Hibiscus plant remained very poor. The wide band gap in the N-719 sensitizer minimizes surface defects of the DSSCs from charge

recombination. Cells with higher DSSCs efficiency exhibit increased V_{OC} values. Because the higher charge-drawing efficiency of light and less charge recombination show the importance of thin film configuration.

The performance results of the DSSCs $TiCl_4$ -treated are presented in Table 5. While positive effects were observed on some of these cells, decreases were recorded in some of them. The cells showing improvements include TiO_2 -H-rGO, 1.0 La TiO_2 -N-rGO and 1.0 Yb TiO_2 -N-rGO. The

application of $TiCl_4$ for surface passivation on the mesoporous TiO_2 layer in DSSCs was obtained with the highest 3.78% efficiency among the cells produced, with N719 as a 1.0 M La doped dye and rGO components in the cathode (1.0 La TiO_2 ($TiCl_4$)-N-rGO).

Table 7 presents the performance data of the DSSCs using Pt in the CE. The efficiency of the cell using rGO and the cell using Pt were equal at 1.5%. This similarity in efficiency is attributed to the higher conductivity of rGO

Table 4 Performance results of DSSC of REE-doped TiO_2 thin films with properties given in Table 1

Cell Code	V_{OC} (V)	J_{SC} (mA/cm ²)	P_{MAX}	FF	PCE (η) (%)
0.5 Ho TiO_2 -N-rGO	0,71	11,6	0,33	0,41	1,71
1.0 Ho TiO_2 -N-rGO	0,77	17,8	0,56	0,41	2,87
1.5 Ho TiO_2 -N-rGO	0,79	11,6	0,44	0,48	2,25
1.0 Ho TiO_2 -H-rGO	0,58	0,86	0,03	0,59	0,15
0.5 Er TiO_2 -N-rGO	0,77	5,92	0,23	0,50	1,17
1.0 Er TiO_2 -N-rGO	0,75	13	0,48	0,49	2,42
1.5 Er TiO_2 -N-rGO	0,79	12,64	0,48	0,48	2,44
1.0 Er TiO_2 -H-rGO	0,59	0,63	0,03	0,79	0,15
1.0 La TiO_2 -N-rGO	0,75	9,08	0,36	0,53	1,85
1.0 La TiO_2 -H-rGO	0,61	0,54	0,03	0,84	0,14
1.0 Yb TiO_2 -N-rGO	0,77	5,0	0,20	0,53	1,04
1.0 Yb TiO_2 -H-rGO	0,6	0,53	0,03	0,87	0,14

Table 5 Performance results of $TiCl_4$ treated DSSCs

Cell Code	V_{OC} (V)	J_{SC} (mA/cm ²)	P_{MAX}	FF	PCE (η) (%)
TiO_2 ($TiCl_4$)-N-rGO	0,72	5,91	0,00-024	0,56	1,22
TiO_2 ($TiCl_4$)-H-rGO	0,53	0,53	1,5-8 × 10 ⁻⁵	0,56	0,25
1.0 Ho TiO_2 ($TiCl_4$)-N-rGO	0,75	9,03	0,00-032	0,47	1,62
1.0 La TiO_2 ($TiCl_4$)-N-rGO	0,75	17,04	0,00-074	0,58	3,78
1.0 Er TiO_2 ($TiCl_4$)-N-rGO	0,74	8,85	0,00-030	0,46	1,55
1.0 Yb TiO_2 ($TiCl_4$)-N-rGO	0,65	6,99	0,00-022	0,49	1,13

compared to graphene oxide. rGO contributes to this result with its high surface/volume ratio and excellent electronic transport properties [97].

3.9 Incident photon to current conversion efficiency (IPCE) of DSSCs using pure and REEs doped TiO₂ film synthesized by sol-gel method

IPCE, which measures the number of electrons generated by a solar cell in response to photons incident on its active surface under monochromatic light in the UV and visible

light range (300–700 nm), provides crucial data for evaluating the performance of the DSSCs. IPCE graphs are presented in Figs. 23–26.

In Fig. 23a, it is observed that the S-H-GO cell-coded DSSCs absorb in the 300–400 nm range and its highest efficiency is 4.04% at 349 nm, while the S-N-GO cell reaches its highest efficiency at 5.4% at 330 nm. In addition, in (b), the S-H-rGO cell-coded DSSCs absorb in the 300–400 nm range and its highest efficiency is 4.09% at 350 nm, while the highest efficiency of the S-N-rGO cell is measured as 6.15% at 334 nm.

Figure 24a shows that the 1.0 Ho-N-rGO cell absorbs light in the 300–400 nm range and the highest efficiency is 24.3% at 330 nm, while the 1.0 Ho-H-rGO cell absorbs 3.19% at 330 nm. Also, it is seen in Fig. 24b that the 0.5 Ho-N-rGO cell absorbs between 300 and 400 nm and reaching a maximum efficiency of 7.5% at 327 nm, while the 1.5 Ho-N-rGO cell achieves an efficiency of 13.32% at 340 nm.

Figure 25a shows that the Er-N-rGO cell absorbs light in the 300–400 nm range, reaching a maximum efficiency of 17.69% at 330 nm, whereas the 1.0 Er-H-rGO cell achieves an efficiency of 5.44% at the same wavelength. Figure 25b also shows that the 0.5 Er-N-rGO cell absorbs light in the 300–400 nm range, reaching a maximum efficiency of 10.0% at 350 nm, whereas the 1.5 Er-N-rGO cell achieves an efficiency of 11.0% at 316 nm.

Figure 26a shows that the 1.0 Yb-N-rGO cell absorbs light in the 300–400 nm range, reaching a maximum

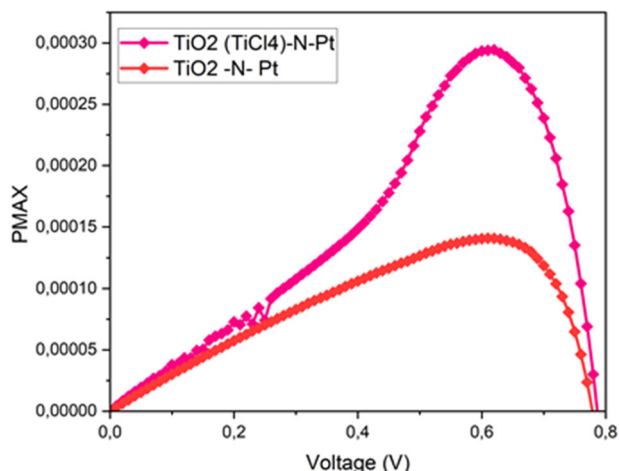


Fig. 22 Pmax-V graph of DSSCs using Pt in the photocathode

Table 6 Performance results of DSSCs using Pt in photocathode

Hücre Kodu	V _{OC} (V)	J _{SC} (mA/cm ²)	P _{MAX}	FF	PCE (η) (%)
TiO ₂ (TiCl ₄)-N-Pt	0,78	1,61	$1,41 \times 10^{-4}$	0,99	0,72
TiO ₂ -N-Pt	0,74	2,13	$2,95 \times 10^{-4}$	0,99	1,5

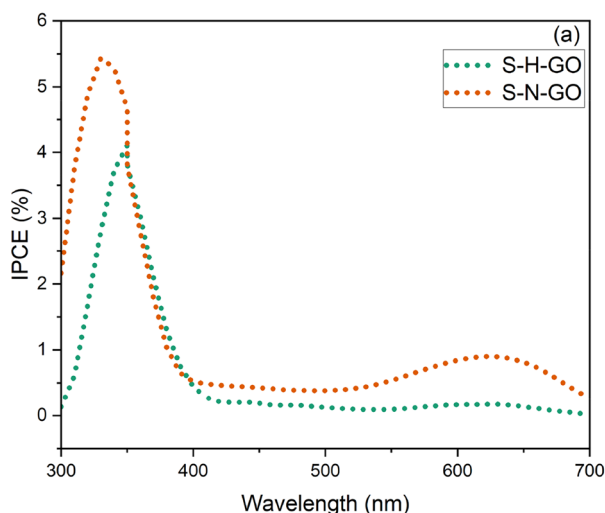
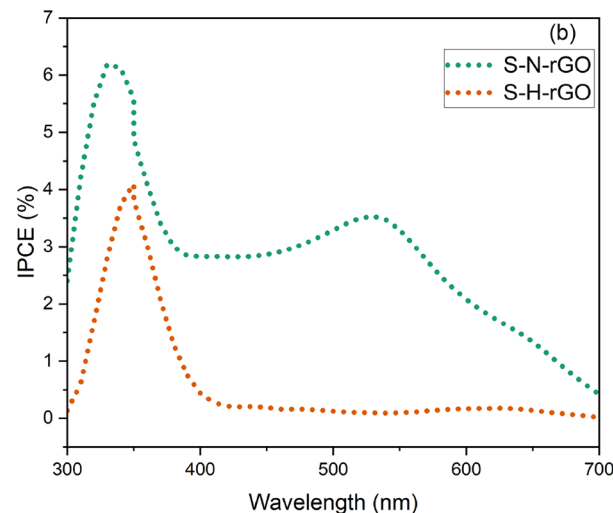
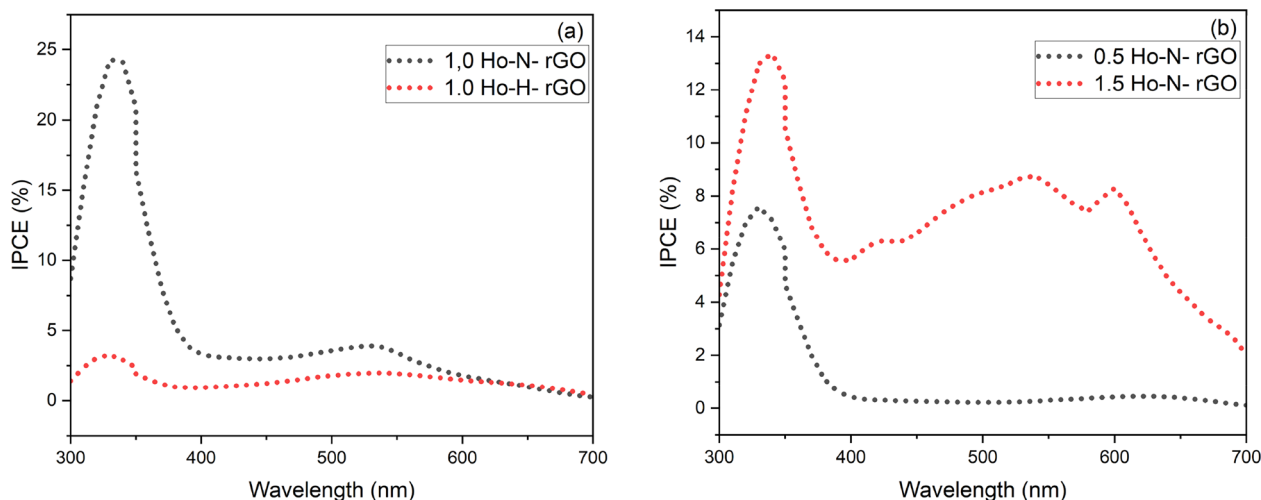
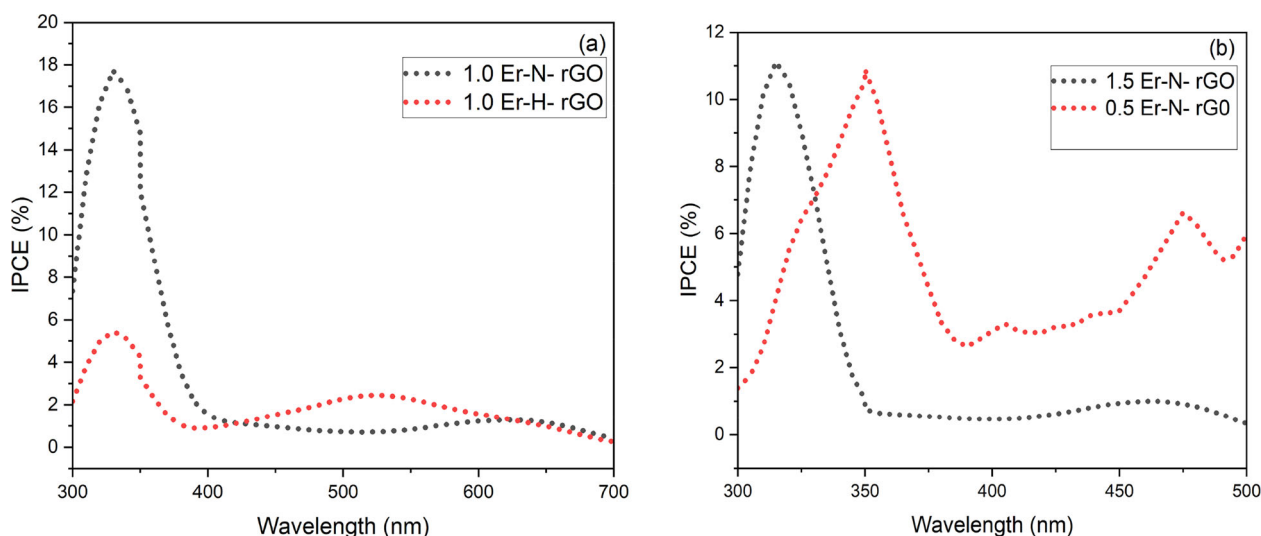


Fig. 23 Photon-current conversion efficiency of (a) S-N-GO, S-H-GO, b S-N-rGO and S-H-rGO DSSCs

Table 7 Incident Photon to Current Conversion Efficiency (IPCE) of DSSCs Using Pure and REE Doped TiO₂ Film

Cell No	Cell components	Cell code	IPCE (%)
1	TiO ₂ -N719-GO	S-N-GO	5,4
2	TiO ₂ -Hibiscus-GO	S-H-GO	4,04
3	TiO ₂ -N719-rGO	S-N-rGO	6,15
4	TiO ₂ -Hibiscus-rGO	S-H-rGO	4,09
5	%1,0 M Ho TiO ₂ -N719-rGO	1.0 Ho-N- rGO	24,3
6	%1,0 M Ho TiO ₂ -Hibiscus-rGO	1.0 Ho-H- rGO	3,19
7	%0,5 M Ho TiO ₂ -N719-rGO	0.5 Ho-N- rGO	7,5
8	%1,5 M Ho TiO ₂ -N719-rGO	1.5 Ho-N- rGO	13,32
9	%1,0 M Er TiO ₂ -N719-rGO	1.0 Er-N- rGO	17,69
10	%1,0 M Er TiO ₂ -Hibiscus-rGO	1.0 Er-H- rGO	5,44
11	%0,5 M Er TiO ₂ -N719-rGO	0.5 Er-N- rGO	10,0
12	%1,5 M Er TiO ₂ -N719-rGO	1.5 Er-N- rGO	11,0
13	%1,0 M La TiO ₂ -N719-rGO	1.0 La-N- rGO	10,4
14	%1,0 M La TiO ₂ -Hibiscus-rGO	1.0 La-H- rGO	3,2
15	%1,0 M Yb TiO ₂ -N719-rGO	1.0 Yb-N- rGO	12,14
16	%1,0 M Yb TiO ₂ -Hibiscus-rGO	1.0 Yb-H- rGO	6,2

**Fig. 24** Photon-current conversion efficiency of (a) 1.0 Ho-N-rGO, 1.0 Ho-H-rGO, b 0.5 Ho-N-rGO and 1.5 Ho-N-rGO DSSCs**Fig. 25** Photon-current conversion efficiency of (a) 1.0 Er-N-rGO, 1.0 Er-H-rGO, b 0.5 Er-N-rGO and 1.5 Er-N-rGO DSSCs

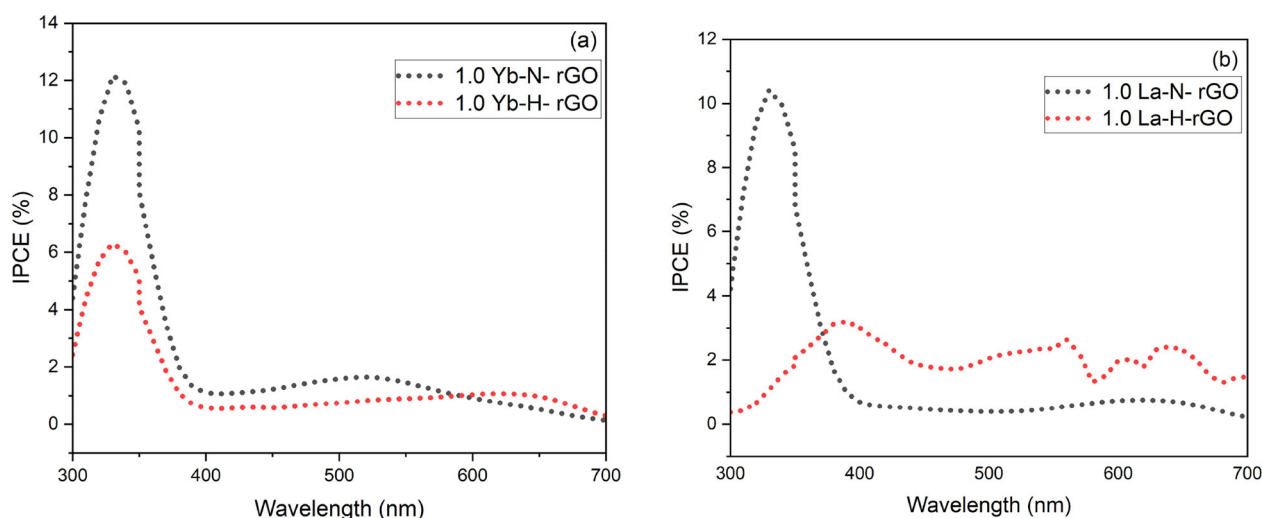


Fig. 26 Photon-current conversion efficiency of (a) 1.0 Yb-N-rGO and 1.0 Yb-H-rGO b 1.0 La-N-rGO and 1.0 La-H-rGO DSSCs

efficiency of 12.14% at 330 nm, whereas the 1.0 Yb-H-rGO cell absorbs mainly at 330 nm and achieves an efficiency of 6.2% at the same wavelength. Figure 26b also shows that the 1.0 La-N-rGO cell absorbs light in the 300–400 nm range, reaching a maximum efficiency of 10.4% at 328 nm, whereas the 1.0 La-H-rGO cell absorbs mainly at 386 nm and achieves an efficiency of 3.2% at 328 nm.

According to the data in Table 7, the highest value for DSSCs devices was obtained for the sample doped with 1.0% Ho^{+3} and these values confirm and agree with the DSSCs efficiency (I-V) characterization measurements. The strong response to visible light at 300–400 nm wavelength. Moreover, because the IPCE response appeared weak in the near-infrared wavelength region, that range was not shown for some samples. Another reason for the quantum efficiency losses in the above regions may be the defects (trap states) that cause the recombination of holes and electrons. Moreover, as understood from the results, the photons coming onto the DSSCs were converted into current more effectively with doping.

By examining the table, the changes in IPCE (%) values with different TiO_2 components, forms of graphene oxide (GO and rGO), and metal dopants can be observed. Firstly, among the cells without metal doping, TiO_2 -N719-rGO exhibits the highest IPCE value of 6.15%. In contrast, TiO_2 -Hibiscus-GO shows a lower IPCE of 4.04%. This suggests that TiO_2 -N719-based cells are more effective in terms of photon absorption and conversion efficiency compared to TiO_2 -Hibiscus-based cells. The impact of Ho doping is particularly notable. 1.0 M Ho TiO_2 -N719-rGO achieves a significant increase in IPCE to 24.3%, indicating that Ho doping has a substantial positive impact on the TiO_2 -N719-rGO system. In contrast, 1.0 M Ho TiO_2 -Hibiscus-rGO exhibits a much lower IPCE of 3.19%, demonstrating that

Ho doping significantly improves the TiO_2 -N719-based cell but has a much less pronounced effect on the TiO_2 -Hibiscus system. For other Ho concentrations, 0.5 M Ho TiO_2 -N719-rGO and 1.5 M Ho TiO_2 -N719-rGO achieve IPCE values of 7.5% and 13.32%, respectively, both of which are higher than 1.0 M Ho TiO_2 -Hibiscus-rGO, further confirming that TiO_2 -N719-rGO benefits more from Ho doping compared to TiO_2 -Hibiscus.

The effect of Er doping is also notable. The 1.0 M Er TiO_2 -N719-rGO cell exhibits an IPCE of 17.69%, indicating that Er doping enhances efficiency, although not as markedly as Ho doping. In contrast, 1.0 M Er TiO_2 -Hibiscus-rGO shows an IPCE of 5.44%, indicating that this doping has a more limited effect in the TiO_2 -Hibiscus-based cells.

Doping with La and Yb yields more moderate results. 1.0 M La TiO_2 -N719-rGO exhibits an IPCE of 10.4%, which is a positive increase, but still lower compared to Ho and Er doping. Both 1.0 M La TiO_2 -Hibiscus-rGO and 1.0 M Yb TiO_2 -Hibiscus-rGO exhibit IPCE values of 3.2% and 6.2%, respectively, showing that La and Yb doping do not result in significant improvements for the Hibiscus-based cells.

In conclusion, Ho doping provides the most significant enhancement in IPCE, particularly in TiO_2 -N719-rGO cells, with the highest recorded IPCE of 24.3%. Er and Yb doping also enhance IPCE but not to the same extent as Ho. La doping does not lead to a notable improvement in efficiency. In addition, as understood from the results, the photons coming to the DSSCs are converted into current more effectively by doping. Overall, the TiO_2 -N719 cells out performs the TiO_2 -Hibiscus composition in terms of IPCE, except in the case of Ho doping in TiO_2 -Hibiscus.

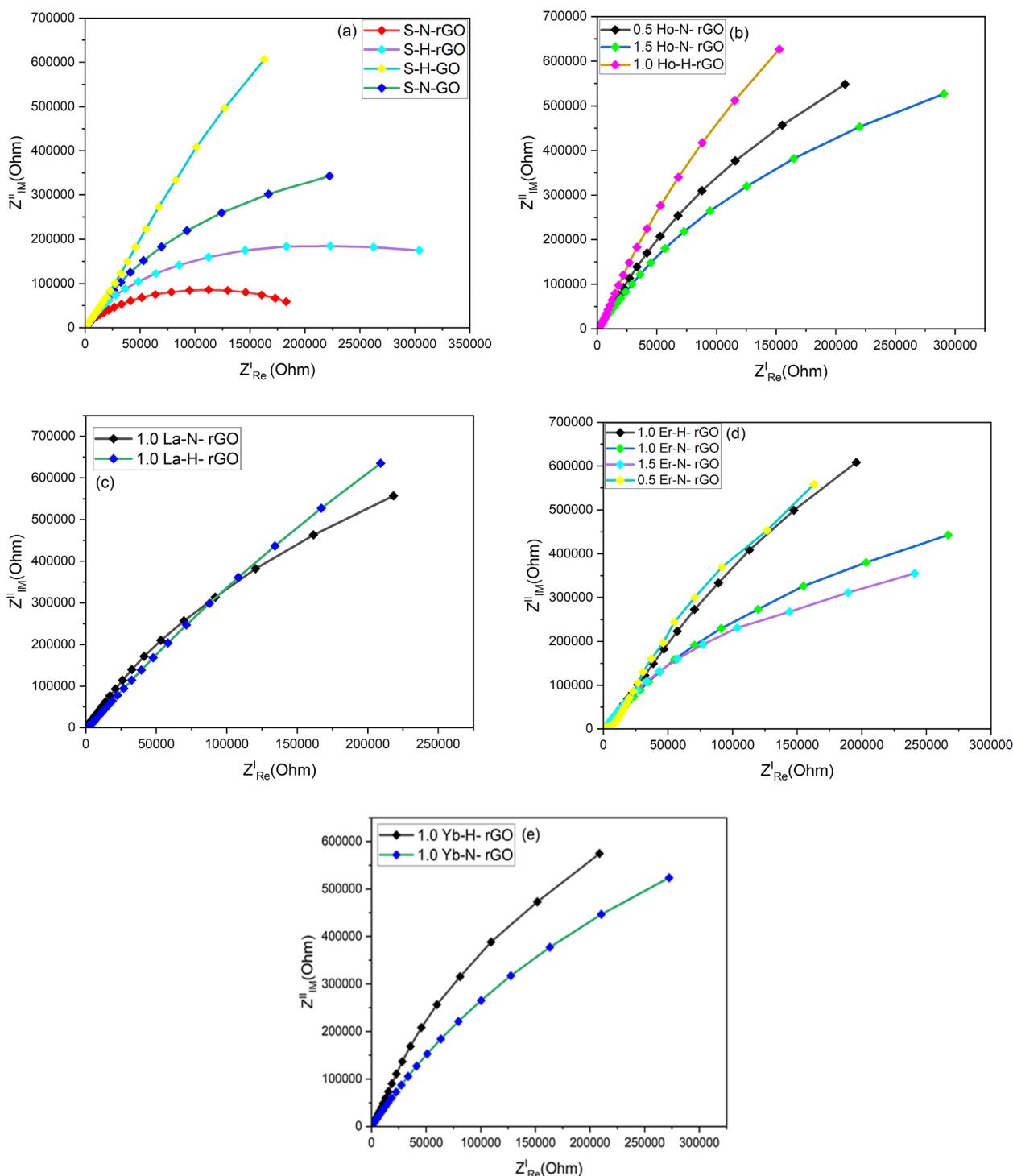


Fig. 27 Nyquist diagrams of **a** undoped, **b** Ho-doped, **c** La-doped, **d** Er-doped and **e** Yb-doped DSSCs

3.10 Electrochemical impedance spectroscopy (EIS) analysis of DSSCs using pure and REEs doped TiO_2 thin film as photoanode

EIS measurements are used as an effective method to deeply investigate the kinetics of photoelectrochemical processes including ionic and electronic activities in DSSCs. EIS

measurements of DSSCs was performed with a potentiostat/galvanostat in the frequency range of 10^{-2} - 10^5 Hz at room temperature and under dark conditions. The V_{oc} value of DSSCs with an applied bias voltage and an alternating current (AC) amplitude of 10 mV was adjusted. The obtained EIS spectra were simulated with the software of the device and the most suitable equivalent circuit was fitted

Table 8 Resistance values of DSSCs

Cell Code	R_s (Ω)	$C1$ (μF)	$R1$ (10^3) (Ω)	Q (10^{-6})	$R2$ (10^3) (Ω)	$C2$ (μF)	$R3$ (10^6) (Ω)
S-N-GO	14,2	21,92	22,9	21,13	63,2	46,04	0,121
S-H-GO	17,71	17,72	0282	45,21	14,1	30, 69	0,672
S-N-rGO	10,07	37,09	0,091	18,06	441,7	27,44	0,0005
S-H-rGO	12,06	24,05	0,017	31,33	43,7	20,28	0,0009
0.5 Ho-N-rGO	16,12	26,14	0,725	20,14	38,8	62,57	1,825
1.0 Ho-H-rGO	18,84	33,16	4,965	16,59	27,4	18,45	0,935
1.5 Ho-N-rGO	13,74	41,21	0,234	29,88	36,9	44,06	0,972
0.5 Er-N-rGO	12,09	34,13	0,460	23,55	3,4	12,07	0,0003
1.0 Er-N-rGO	12,97	42,14	17,888	16,54	3,0	24,04	0,0002
1.0 Er-H-rGO	23,52	40,41	2,504	19,11	5,8	32,75	0,0002
1.5 Er-N-rGO	11,31	43,54	1,784	10,78	11,1	23,35	0,0005
1.0 La-N-rGO	8,165	27,09	12,278	41,79	20,3	64,76	0,0401
1.0 La-H-rGO	13,3	19,13	1,893	9,867	21,0	32,41	0,0112
1.0 Yb-N-rGO	9,996	19,34	2,189	38,41	10,7	23,37	1,602
1.0 Yb-H-rGO	10,35	17,95	9,913	22,88	2,25	42,81	2,117

Table 9 1.0% M Ho TiO₂-N719-rGO DSSC resistance values

Cell Code	R_s (Ω)	$Q1$	$R1$ (Ω)	$Q2$ (10^{-6})	$R2$ (Ω)
1.0 Ho-N-rGO	8,33	2,602	7620	15,24	1245

to the Nyquist diagrams. Nyquist diagrams of DSSCs are presented in Fig. 27. The resistance values of each element in the equivalent circuit were determined with the EC-Lab software and these values are provided in Tables 8 and 9. The tables given below presents the resistance values for various Dye-Sensitized Solar Cells (DSSCs) with different compositions, including TiO₂-N719 or TiO₂-Hibiscus, graphene oxide (GO) or reduced graphene oxide (rGO), and doping with metals such as Ho, Er, La, and Yb. The listed parameters include series resistance (R_s), capacitances ($C1$ and $C2$), resistances ($R1$, $R2$, $R3$), and the constant Q , all of which are important for analyzing the performance and stability of these solar cells.

In the circuit model presented in Fig. 28a, R_s denotes the series resistance including the sheet resistance of the TCO glass and the contact resistance of the electrolyte with the cell. In the circuit, $C1//R1$ corresponds to the impedance component of the FTO/TiO₂/Electrolyte interface, $Q//R2$ represents the resistance of the electrolyte, and $C2//R3$ represents the impedance component of the FTO/RGO/Electrolyte interface. The capacitive fixed phase elements C and Q describe the electrical behavior at these interfaces.

The primary interfaces in a DSSCs are: FTO/TiO₂/dye/electrolyte, TiO₂/dye/electrolyte, and electrolyte/rGO/FTO. These interfaces are represented by the resistances $R1$, $R2$, and $R3$, respectively. Additionally, the total series resistance of the cell denoted as R_s , which serves as a parameter that

shifts the starting point of the semicircles in the impedance plot [98]. The equivalent circuit model that fits the DSSCs is consistent with the studies of Ezema et al. (2016) and Lohar et al. (2020) [99, 100].

Among all these cells, the 1.0 Ho-N-rGO cell exhibited the lowest charge transfer resistance as illustrated in Fig. 27f. This indicates, it proved that it has high catalytic activity and better charge transfer capability. The 1.0 Ho-N-rGO cell differed from the other cells as shown in Fig. 27f. The power efficiency of this cell also showed the best performance with 2.87% without TiCl₄ treatment. The equivalent circuit elements of the 1.0 Ho-N-rGO cell whose circuit model is shown in Fig. 28b have the following meanings: R_s is the series resistance or a solution resistance, $R1//Q1$ represents the impedance at the TiO₂/dye/electrolyte interface, while the impedance at the CE/electrolyte interface is represented by $R2//Q2$. The real part of the impedance is represented by $R1$ and $R2$, while the constant phase element (CPE) are denoted by $Q1$ and $Q2$ [100]. Charge transfer resistance is a key factor in solar cell efficiency.

Comparison of the 1.0% M Ho TiO₂-N719-rGO cell to the earlier 1.0 Ho-N-rGO from the previous table, reveals a significant decrease in series resistance (R_s) in the 1.0% M Ho TiO₂-N719-rGO, which is generally favorable for efficient operation. However, the increased $R1$ and $R2$ values indicate higher resistance in the charge transport path and overall reduced efficiency in terms of charge transfer, compared to the earlier 1.0 Ho-N-rGO configuration. Additionally, the lower $Q1$ and $Q2$ values in this configuration suggest faster charge dynamics, potentially at the expense of charge storage capacity. Overall, although the lower R_s is beneficial, the higher resistances in $R1$ and $R2$

Fig. 28 **a** Circuit model of DSSCs. **b** Circuit model of 1.0% M Ho TiO₂-N719-rGO DSSC

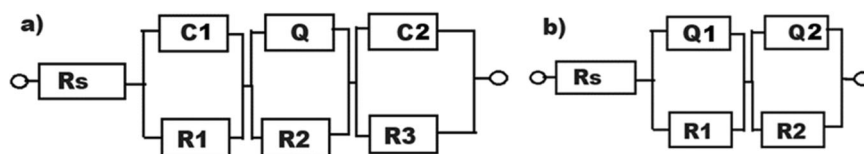


Table 10 1.0% M Ho TiO₂-N719-rGO DSSC resistance values

Cell Code	R_s (Ω)	Q1	R1 (Ω)	Q2 (10^{-6})	R2 (Ω)
1.0 Ho-N-rGO	8,33	2,602	7620	15,24	1245

may offset these gains, making the 1.0% M Ho TiO₂-N719-rGO cell potentially less efficient than the previously observed 1.0 Ho-N-rGO configuration. Further optimization of doping concentration or material composition may be required to achieve an optimal balance between charge transport and charge retention.

4 Conclusions

In this study, TiO₂ photoanodes used in DSSCs and their properties are investigated. The surface area and porosity of TiO₂ are key factors for achieving high efficiency in DSSCs. The high specific surface area of TiO₂ enhances light harvesting, allowing for more dye adsorption, which in turn enhances the efficiency of photochemical reactions. Additionally, the effects of doping TiO₂ with REEs (Ho³⁺, La³⁺, Er³⁺ and Yb²⁺) to enhance the surface properties of TiO₂ photoanodes and the use of rGO as an alternative to Pt in the CE are also explored in this study. The results reveal important findings summarized below.

- The doping process improved the crystal structure and optical properties of TiO₂, with the doping of Ho³⁺, La³⁺, Er³⁺, and Yb²⁺ significantly enhancing the light absorption properties and photovoltaic performance of TiO₂. Specifically, the 1.0% Ho³⁺ doped TiO₂-N-rGO cell exhibited the highest performance with an efficiency of 2.87%. This result demonstrates that lanthanides create additional crystal defects and surface active sites, which help prevent electron-hole pair recombination and enhance the chemical adsorption of organic compounds on the electrode surface.
- The optical properties of DSSCs were investigated using spectroscopic analysis in the UV and visible light ranges, revealing that doping reduces the bandgap of TiO₂, allowing for more photon absorption.
- BET analysis was performed to evaluate the changes in surface area and pore size of pure TiO₂ and 1.0% RRE doped TiO₂ used as photoanodes. TiO₂ nanostructures with high surface area and narrow pore size distribution

allow more dye loading and more efficient electrolyte leakage when used as photoanodes in DSSCs. 1.0% Ho TiO₂ cell has 111.07 m²/g surface area, 166.32 nm average particle size and 16.37 nm pore size, and it is confirmed by the fact that it achieves better PCE compared to other photoanodes.

- Comparison of the light absorption spectra of the N-719 dye and the natural dye extracted from hibiscus plants, revealed that N-719 exhibited strong absorption over a wider spectral range, thereby enhancing the efficiency of DSSCs.
- Surface passivation with TiCl₄ was found to improve efficiency in some cells but did not show positive effects in all cells. Efficiency was enhanced, notably in the TiO₂-H-rGO, 1.0% La TiO₂-N-rGO, and 1.0% Yb TiO₂-N-rGO cells.
- Additionally, cells using rGO demonstrated higher efficiency compared to those using GO, as rGO has higher electrical conductivity.
- EIS analysis provided detailed insights into the charge transport characteristics of the DSSCs. The 1.0% Ho-N-rGO cell exhibited superior catalytic activity with low charge transfer resistance, showing the best performance in terms of efficiency. This cell demonstrated distinct performance in charge transfer and efficiency relative to other cells.
- IPCE analysis was further employed to examine the photovoltaic performance of the DSSCs in greater detail. Doped cells demonstrated higher over a broader light absorption range, enabling more effective photon conversion. Cells with N-719 dye exhibited higher IPCE values than those with the hibiscus-derived natural dye.

In conclusion, this study demonstrates that enhancing the surface properties of TiO₂ photoanodes through REEs doping and using rGO as alternatives to Pt in the CE significantly improves the efficiency of DSSCs. Lanthanides doping can improve the photovoltaic performance of TiO₂, while rGO increases the electrical conductivity of the cell. The highest efficiency was achieved in the 1.0% Ho³⁺ doped TiO₂-N-rGO cell, and indicating that effective strategies for enhancing the efficiency of TiO₂ photoanodes have been identified.

Data availability

No datasets were generated or analysed during the current study.

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1007/s10971-026-07134-y>.

Acknowledgements This research was supported by Atatürk University Scientific Research Projects Coordination Unit (BAP) with Project No. FDK-2021-8885.

Author contributions BC: Conceptualization, Investigation, Methodology, Supervision, Project administration, Writing—original, Writing—review & editing. ES: Conceptualization, Supervision, Project administration, Writing—review & editing. EI: Supervision, Writing—review & editing. All authors reviewed the manuscript.

Funding Atatürk University Scientific Research Projects Coordination Unit (BAP), Project No. FDK-2021-8885. Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK).

Conflict of interest The authors declare no competing interests.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Saravanan KK, Venkatesan D, Regan R, Hariharan G (2025) Optimizing dye-sensitized solar cells with a TiO₂/CoS hybrid photoanode for enhanced solar energy conversion. *Ionics* (Kiel). <https://doi.org/10.1007/s11581-025-06125-3>.
- Ansari AA, Nazeeruddin MK, Tavakoli MM (2021) Organic-inorganic upconversion nanoparticles hybrid in dye-sensitized solar cells *Coord Chem Rev* 436:1
- Aljafari B, James S, Sorrentino A, Anandan S (2024) Nanostructured g-C₃N₄-decorated TiO₂ for superior photoanode performance in dye-sensitized solar cells. *Inorg Chem Commun* 159: <https://doi.org/10.1016/j.inoche.2023.111737>.
- Varga Z, Racz E (2023) Statistical Analysis of the Performance of the Dye-Sensitized Solar Cell - Thermoelectric Generator. In: 2023 IEEE 21st World Symposium on Applied Machine Intelligence and Informatics, SAMI 2023 - Proceedings. Institute of Electrical and Electronics Engineers Inc., 267–272.
- Ayub M, Shahzad N, Javed AH (2024) Performance evaluation of ruthenium complexes and organic sensitizers in ZnO-based dye-sensitized solar cells. *Eng Res Expr* 6. <https://doi.org/10.1088/2631-8695/ad5787>.
- Bezabih MS (2024) Nanocomposite counter-electrode materials for dye-sensitized solar cells: A review *Energy Technol* 12:1
- Zheng D, Yang X, Čuček L, Wang J, Ma T, Yin C (2024) Revolutionizing dye-sensitized solar cells with nanomaterials for enhanced photoelectric performance. *J Clean Prod* 464:142717. <https://doi.org/10.1016/j.jclepro.2024.142717>.
- Ullah N, Shuja A, Shah SM, Ansir R, Alrashidi KA, Mohammad S (2024) Enhancing dye-sensitized solar cells efficiency through organic dyes-sensitized holmium-doped TiO₂/SnO₂ nanocomposites blended with P3HT. *Opt Mater (Amst)* 157:116255. <https://doi.org/10.1016/j.optmat.2024.116255>.
- Bahutair WN, Alhajar A, Othman AAL, Tawalbeh M (2024) The role of MXenes and MXene composites in enhancing dye-sensitized solar cells characteristics. *Process Saf Environ Prot* 191:490–504.
- Rajkumar S, Venkatraman MR, Arunkumar A, Jayaprakash K (2025) Anthocyanin and betalain pigments assisted green synthesis of TiO₂: A sustainable and cost-effective approach for dye-sensitized solar cells photoanodes. *Opt Mater (Amst)* 160: <https://doi.org/10.1016/j.optmat.2025.116710>.
- Amalina AN, Benu DP, Setiawan KM, Nurhayati, Steky FV, Milana P (2024) Shedding light on N719 dye adsorption mechanisms on Degussa (Evonik) P25 TiO₂ nanoparticles towards dye-sensitized solar cell performance. *Powder Technol* 446:120087. <https://doi.org/10.1016/j.powtec.2024.120087>.
- Kraidy AF, Yapi AS, Saint-Gregoire P, Vaillant-Roca L, Eke S, Mouangue R (2024) Enhancement of natural dye-sensitized solar cell efficiency through TiO₂ Hombikat UV100 and TiO₂ P25 photoanode optimization. *Processes* 12:2481. <https://doi.org/10.3390/pr12112481>.
- Zhang Y, Tao H, Wang H, et al. (2025) Sol-gel synthesis of magnesium doped TiO₂ thin film and its application in dye sensitized solar cell. *Opt Mater (Amst)* 158. <https://doi.org/10.1016/j.optmat.2024.116446>.
- Mahshid S, Askari M, Ghamsari MS (2007) Synthesis of TiO₂ nanoparticles by hydrolysis and peptization of titanium isopropoxide solution. *J Mater Process Technol* 189:296–300. <https://doi.org/10.1016/j.jmatprotec.2007.01.040>.
- Koo BR, Oh DH, Ahn HJ (2018) Influence of Nb-doped TiO₂ blocking layers as a cascading band structure for enhanced photovoltaic properties. *Appl Surf Sci* 433:27–34. <https://doi.org/10.1016/j.apsusc.2017.10.078>.
- Aarik J, Aidla A, Uustare T, Sammelselg V (1995) 268-275 Morphology and structure of TiO₂ thin films grown by atomic layer deposition.
- Aslan F (2024) New natural dyes extracted by ultrasonic and soxhlet method: Effect on dye-sensitized solar cell photovoltaic performance. *Opt Quantum Electron* 56: <https://doi.org/10.1007/s11082-024-06294-x>.
- Rajendhiran R, Atchudan R, Palanisamy J, Balasankar A, Oh TH, Deivasigamani V (2023) Prickly pear fruit extract: Capping agent for the sol-gel synthesis of discrete titanium dioxide nanoparticles and sensitizer for dye-sensitized solar cell. *Coatings* 13:579. <https://doi.org/10.3390/coatings13030579>.
- Hajizadeh-Oghaz M (2019) Synthesis and characterization of Nb-La co-doped TiO₂ nanoparticles by sol-gel process for dye-sensitized solar cells. *Ceram Int* 45:6994–7000. <https://doi.org/10.1016/j.ceramint.2018.12.200>.
- Hočevár M, Krašovec UO, Bokalič M, Topič M, Veurman W, Brandt H (2013) Sol-gel based TiO₂ paste applied in screen-printed dye-sensitized solar cells and modules. *J Ind Eng Chem* 19:1464–1469. <https://doi.org/10.1016/j.jiec.2012.12.046>.
- Shakya MDPA, Jayathilaka KMDC, Fernando WTRS, Wanninayake WTMAPK, Kumara LSR, Seo O et al. (2025) A Study on Cu Thin-Film Electroplated TiO₂ Photoanodes for Applications in Natural Dye-Sensitized Solar Cells. *Cryst (Basel)* 15:28. <https://doi.org/10.3390/cryst15010028>.
- Joshay D, Narendranath SB, Ismail YA, Periyat P (2022) Recent progress in one dimensional TiO₂ nanomaterials as photoanodes in dye-sensitized solar cells. *Nanoscale Adv* 73:5207–5208.

23. Du P, Lim JH, Leem JW, Cha SM, Yu JS (2015) Enhanced Photovoltaic Performance of Dye-Sensitized Solar Cells by Efficient Near-Infrared Sunlight Harvesting using Upconverting Y2O3:Er3+/Yb3+ Phosphor Nanoparticles. *Nanoscale Res Lett* 10:1030. <https://doi.org/10.1186/s11671-015-1030-0>.
24. Yao N, Huang J, Fu K, Deng X, Ding M, Xu X (2016) Rare earth ion doped phosphors for dye-sensitized solar cells applications. *RSC Adv* 6:17546–17559.
25. Hossain MK, Raihan GA, Akbar MA, Kabir Rubel MH, Ahmed MH, Khan MI (2022) Current applications and future potential of rare earth oxides in sustainable nuclear, radiation, and energy devices: A review. *ACS Appl Electron Mater* 4:3327–3353.
26. Sun J, Yang X, Sun S, et al (2022) Recent progress of rare earth conversion material in perovskite solar cells: A mini review. *Inorg Chem Commun* 143:7.
27. Miao C, Chen C, Dai Q, Xu L, Song H (2015) Dysprosium, Holmium and Erbium ions doped Indium Oxide nanotubes as photoanodes for dye sensitized solar cells and improved device performance. *J Colloid Interface Sci* 440:162–167. <https://doi.org/10.1016/j.jcis.2014.10.055>.
28. Arslan H, Anabilim Dah F SELÇUK ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ EVROPIYUM (Eu +3) KATKILI TiO2 İNCE FİLMLERİN SENTEZİ KARAKTERİZASYONU VE BOYA DUYARLI GÜNEŞ PİLİNDE FOTO-ANOT OLARAK KULLANIMI Eylül-2018 KONYA Her Hakkı Saklıdır.
29. Khannam M, Dolui SK (2017) Cerium doped TiO2 photoanode for an efficient quasi-solid state dye sensitized solar cells based on polyethylene oxide/multiwalled carbon nanotube/polyaniline gel electrolyte. *Sol Energy* 150:55–65. <https://doi.org/10.1016/j.solener.2017.04.035>.
30. Farheen, Fouad H, Ansari SG et al. (2017) Europium doped TiO2: an efficient photoanode material for dye sensitized solar cell. *J Mater Sci: Mater Electron* 28:6873–6879. <https://doi.org/10.1007/s10854-017-6387-7>.
31. Yuliantini L, Nursam NM, Pranoto LM, Shobih, Hidayat J, Sovia RR (2023) Photon up-conversion in Er3+ ion-doped ZnO-Al2O3-BaO-B2O3 glass for enhancing the performance of dye-sensitized solar cells. *J Alloy Compd* 954:170163. <https://doi.org/10.1016/j.jallcom.2023.170163>.
32. Markose A, Das D, Ravindran P (2023) Quantitative framework development for understanding the relationship between doping and photoelectrochemical energy conversion of TiO2. *Mater Adv* 4:3399–3451.
33. Tropea A, Spadaro D, Trocino S, Giuffrida D, Salerno T, Ruiz-Sanchez JP (2024) Development of dye-sensitized solar cells using pigment extracts produced by *Talaromyces atrovirens* GH2. *Photochem Photobiol Sci* 23:941–955. <https://doi.org/10.1007/s43630-024-00566-x>.
34. Narayan MR (2012) Review: Dye sensitized solar cells based on natural photosensitizers. *Renew Sustain Energy Rev* 16:208–215.
35. Richhariya G, Kumar A, Tekasakul P, Gupta B (2017) Natural dyes for dye sensitized solar cell: A review. *Renew Sustain Energy Rev* 69:705–718.
36. Abdou EM, Hafez HS, Bakir E, Abdel-Mottaleb MSA (2013) Photostability of low cost dye-sensitized solar cells based on natural and synthetic dyes. *Spectrochim Acta A Mol Biomol Spectrosc* 115:202–207. <https://doi.org/10.1016/j.saa.2013.05.090>.
37. Yadav SC, Sharma A, Devan RS, Shirage PM (2022) Role of different counter electrodes on performance of TiO2 based dye-sensitized solar cell (DSSC) fabricated with dye extracted from Hibiscus Sabdariffa as sensitizer. *Opt Mater (Amst)* 124. <https://doi.org/10.1016/j.optmat.2022.112066>.
38. Shalini S, Balasundaraprabhu R, Satish Kumar T, Muthukumarasamy N, Prasanna S, Sivakumaran K (2018) Enhanced performance of sodium doped TiO2 nanorods based dye sensitized solar cells sensitized with extract from petals of Hibiscus sabdariffa (Roselle). *Mater Lett* 221:192–195. <https://doi.org/10.1016/j.matlet.2018.03.091>.
39. Cao C, Yang T, Chen G (2021) Hibiscus leachate dye-based low-cost and flexible dye-sensitized solar cell prepared by screen printing. *Materials* 14:2748. <https://doi.org/10.3390/ma14112748>.
40. Ramelan AH, Wahyuningsih S, Rosyida NA, Supriyanto E., Saputro S., Hanif Q.A., (2016), 030012 Anthocyanin extracted from Hibiscus (Hibiscus rosa sinensis L.) as a photosensitizer on nanostructured-TiO2 dye sensitized solar cells. In: AIP Conference Proceedings. American Institute of Physics Inc.
41. Ahmad SN, Yahaya NA, Bahsan R, Rozali S (2022) A study on the effect of gold nanoparticles for dye sensitized solar cell using hibiscus rosa-sinensis as photosensitizer. *Int J Integr Eng* 14:238–244. <https://doi.org/10.30880/ijie.2022.14.05.027>.
42. Aziz NAS, Rahman MYA, Umar AA, Mawarnis ER, Zuhdi AWM (2025) Dye-sensitized solar cells utilizing aurum-palladium bimetal film counter electrode. *Ion (Kiel)* 31:2855–2867. <https://doi.org/10.1007/s11581-025-06121-7>.
43. Kawuri KR, Ramelan AH, Supriyanto A, Wahyuningsih S, Harjana H, Fadillah G (2025) Improving the efficiency of dye-sensitized solar cell with reduced graphene oxide-cobalt molybdenum sulfide as counter electrode. *Inorg Chem Commun* 173:113891. <https://doi.org/10.1016/j.inoche.2025.113891>.
44. Senadeera GKR, Weerasekara WMSK, Jaseetharan T, Sandunika PU, Kumari JMKW, Dissanayake MAKL (2025) Efficiency enhancement in dye-sensitized solar cells through neodymium-doped graphene quantum dot-modified TiO2 photoanodes. *Phys B Condens Matter* 699:416797. <https://doi.org/10.1016/j.physb.2024.416797>.
45. Fajarwati FI, Hidayat R, Fadillah G (2024) Synthesis and transformation of graphene-like structures from bamboo waste for photoelectrochemical devices. *Carbon Trends* 15. <https://doi.org/10.1016/j.cartre.2024.100351>.
46. Long D, Li W, Ling L, Miyawaki J, Mochida I, Yoon SH (2010) Preparation of nitrogen-doped graphene sheets by a combined chemical and hydrothermal reduction of graphene oxide. *Langmuir* 26:16096–16102. <https://doi.org/10.1021/la102425a>.
47. Wang H, Sun K, Tao F, Stacchiola DJ, Hu YH (2013) 3D Honeycomb-Like Structured Graphene and Its High Efficiency as a Counter-Electrode Catalyst for Dye-Sensitized Solar Cells. *Angew Chem* 125:9380–9384. <https://doi.org/10.1002/ange.201303497>.
48. Mao W, Wei L, Xu X, Zhao L, Liu J, Zhang Z (2023) One-step hydrothermal preparation of bi-functional NiS2/reduced graphene oxide composite electrode material for dye-sensitized solar cells and supercapacitors. *Int J Hydrog Energy* 48:28377–28389. <https://doi.org/10.1016/j.ijhydene.2023.03.089>.
49. Gemeiner P, Homola T, Hatala M, Mikula M (2020) Low-temperature hydrogen plasma reduction of graphene oxide counter electrodes for printed dye-sensitized solar cells. In: NANOCON Conference Proceedings - International Conference on Nanomaterials. TANGER Ltd., pp 210–214.
50. Birhan D, Tekin D, Kiziltas H (2022) Thermal, photocatalytic, and antibacterial properties of rGO/TiO2/PVA and rGO/TiO2/PEG composites. *Polym Bull* 79:2585–2602. <https://doi.org/10.1007/s00289-021-03914-4>.
51. Li ZY, Shaheer Akhtar M, Hee Kuk J, Kong BS, Yang OB (2012) Graphene application as a counter electrode material for dye-sensitized solar cell. *Mater Lett* 86:96–99. <https://doi.org/10.1016/j.matlet.2012.07.006>.
52. Richhariya G, Kumar A (2018) Fabrication and characterization of mixed dye: Natural and synthetic organic dye. *Opt Mater (Amst)* 79:296–301. <https://doi.org/10.1016/j.optmat.2018.03.056>.
53. Dissanayake MAKL, Senthuran S, Senadeera GKR Efficiency enhancement in dye-sensitized solar cells using hierarchical TiO

- 2 submicron size spheres as a light scattering layer. <https://doi.org/10.1007/s10008-020-04727-7> Published.
54. Sikhvivilu LM, Sinha Ray S, Coville NJ (2009) Influence of bases on hydrothermal synthesis of titanate nanostructures. *Appl Phys A Mater Sci Process* 94:963–973. <https://doi.org/10.1007/s00339-008-4877-4>.
 55. Saini P, Sharma B, Singh M, Tandon RP, Singh SP, Mahapatro AK (2019) Electrical Properties of Self Sustained Layer of Graphene Oxide and Polyvinylpyrrolidone Composite. *Integr Ferroelectr* 202:197–203. <https://doi.org/10.1080/10584587.2019.1674837>.
 56. Zhang J, Liu Z, Zhang L, (2021) Preparation of polyvinylpyrrolidone/graphene oxide/epoxy resin composite coatings and the study on their anticorrosion performance. *J Appl Polym Sci* 138. <https://doi.org/10.1002/app.50596>.
 57. Heidari B, Majdabadi A, Naji L, Ghamsari MS, Fakharan Z, Salmani S (2018) Synergetic effect of Ag/PVP on nonlinear optical characteristic of rGO transparent thin films. *Opt Quantum Electron* 50:267. <https://doi.org/10.1007/s11082-018-1503-3>.
 58. Gong Y, Li D, Fu Q, Pan C (2015) Influence of graphene microstructures on electrochemical performance for supercapacitors. *Prog Nat Sci: Mater Int* 25:379–385. <https://doi.org/10.1016/j.pnsc.2015.10.004>.
 59. Mousa MA, Khairy M, Mohamed HM (2018) Dye-Sensitized Solar Cells Based on an N-Doped TiO₂ and TiO₂-Graphene Composite Electrode. *J Electron Mater* 47:6241–6250. <https://doi.org/10.1007/s11664-018-6530-0>.
 60. Ji T, Wu D, Zhang X, Zhao Y, Xu K (2022) The TiO₂ films with sandwich-type polyoxometalates in dye sensitized solar cells with electron recombination decreasing and dye adsorption increasing. *J Coord Chem* 75:457–471. <https://doi.org/10.1080/00958972.2022.2057848>.
 61. Gorgani M, Kaleji BK (2020) Structural, photocatalytic and surface analysis of Nb/Ag codoped TiO₂ mesoporous nanoparticles. *J Solgel Sci Technol* 96:728–741. <https://doi.org/10.1007/s10971-020-05403-y>.
 62. Ren R, Wen Z, Cui S, Hou Y, Guo X, Chen J (2015) Controllable synthesis and tunable photocatalytic properties of Ti₃+doped TiO₂. *Sci Rep* 5: 10714. <https://doi.org/10.1038/srep10714>.
 63. Liu X, Yang J, Hu L et al. (2020) 001/{101} facets co-exposed TiO₂ microsheet arrays with Lanthanum doping for enhancing photocatalytic CO₂ reduction. *J Mater Sci: Mater Electron* 31:19464–19474. <https://doi.org/10.1007/s10854-020-04479-0>.
 64. Sompalli NK, Das A, Syamal De S, Mohan AM, Deivasigamani P (2020) Mesoporous monolith designs of mixed phased titania codoped Sm³⁺/Er³⁺ composites: A super responsive visible light photocatalysts for organic pollutant clean-up. *Appl Surf Sci* 504:144350. <https://doi.org/10.1016/j.apsusc.2019.144350>.
 65. Ren Y, Han Y, Li Z, Liu X, Zhu S, Liang Y (2020) Ce and Er Co-doped TiO₂ for rapid bacteria- killing using visible light. *Bioact Mater* 5:201–209. <https://doi.org/10.1016/j.bioactmat.2020.02.005>.
 66. Mazierski P, Mikolajczyk A, Grzyb T, Caicedo PNA, Wei Z, Kowalska E (2020) On the excitation mechanism of visible responsible Er-TiO₂ system proved by experimental and theoretical investigations for boosting photocatalytic activity. *Appl Surf Sci* 527:146815. <https://doi.org/10.1016/j.apsusc.2020.146815>.
 67. Sedik A, Ferraria AM, Carapeto AP, Bellal B., Trari M., Outemzabet R. (2017) Characterization of TiO₂ films obtained by a wet chemical process. In: *Journal of Electrical Engineering*, 68. De Gruyter Open Ltd, 31–36.
 68. Zhang Z, Li D, Shi W, Liu Y, Zhang Y, Liu Y et al. (2018) A new up-conversion material of Ho³⁺-Yb³⁺-Mg²⁺ Tri-doped TiO₂ and its applications to perovskite solar cells. *Nanoscale Res Lett* 13: 262. <https://doi.org/10.1186/s11671-018-2681-4>.
 69. Jiang X, Li C, Liu S, Zhang F, You F, Yao C (2017) The synthesis and characterization of ytterbium-doped TiO₂ hollow spheres with enhanced visible-light photocatalytic activity. *RSC Adv* 7:24598–24606. <https://doi.org/10.1039/c7ra02165h>.
 70. Zhang J, Xu LJ, Zhu ZQ, Liu QJ (2015) Synthesis and properties of (Yb, N)-TiO₂ photocatalyst for degradation of methylene blue (MB) under visible light irradiation. *Mater Res Bull* 70:358–364. <https://doi.org/10.1016/j.materresbull.2015.04.060>.
 71. Hao Y, Wang X, Shen J, Yuan J, Wang AJ, Niu L (2016) One-pot synthesis of single-crystal Pt nanoplates uniformly deposited on reduced graphene oxide, and their high activity and stability on the electrocatalytic oxidation of methanol. *Nanotechnology* 27:145602. <https://doi.org/10.1088/0957-4484/27/14/145602>.
 72. Hong L, Hao Y, Yang Y, Yuan J, Niu L (2015) Synthesis of graphene-supported one-dimensional nanoporous Pt based catalysts, and their enhanced performance on methanol electro-oxidation. *Nanotechnology* 26:045604. <https://doi.org/10.1088/0957-4484/26/4/045604>.
 73. Ghosh TN, Bhunia AK, Pradhan SS, (2024) 2D nanomaterial–polymer composite: optical and structural properties along with room temperature enhanced dielectric response and magnetic behaviour of graphene oxide doped polyvinylpyrrolidone nanocomposites. *J Mater Sci: Mater Electr* 35: <https://doi.org/10.1007/s10854-024-12881-1>.
 74. Asl HZ, Rozati SM (2019) High-quality spray-deposited fluorine-doped tin oxide: effect of film thickness on structural, morphological, electrical, and optical properties. *Appl Phys A Mater Sci Process* 125: <https://doi.org/10.1007/s00339-019-2943-8>.
 75. Hafedh A, Mohammed M, Ozturk A, Park J (2018) Synthesis of Photocatalytic Titanium Dioxide Nanopowders Using Different Acid Catalysts. *Int J Mech Prod Eng* 6:48–51.
 76. Manikandan K, Thirugnanasundar A, Jafar Ahamed AJA (2019) The investigation on structural, optical and morphological behavior of pure and co-doped TiO₂ nanoparticles developed via sol-gel approach for biological activity. *Mater Res Expr* 6. <https://doi.org/10.1088/2053-1591/ab73f9>.
 77. Rabi S, A atul (2019) Experimental Study of TiO₂ Nanoparticles Fabrication by Sol-gel and Co-precipitation Methods for TiO₂/SnO₂ Composite Thin Film as Photoanode. *J ILMU DASAR*, 20:61–66. <https://doi.org/10.19184/jid.v20i1.9154>.
 78. Ma J, Yang H-L, Ren W-H (2019) Functionalized reduced graphene oxide loaded aligned carbon nanotube layer used as counter electrode for dye-sensitized solar cells. *J Nanosci Nanotechnol* 20:1749–1755. <https://doi.org/10.1166/jnn.2020.17148>.
 79. Madurai Ramakrishnan V, N M, P B, Pitchaiya S, Velauthapillai D, Pugazhendhi A (2020) Transformation of TiO₂ nanoparticles to nanotubes by simple solvothermal route and its performance as dye-sensitized solar cell (DSSC) photoanode. *Int J Hydrog Energy* 45:15441–15452. <https://doi.org/10.1016/j.ijhydene.2020.04.021>.
 80. Tasic N, Marinkovic-Stanojevic Z, Brankovic Z, Zunic M, Lacnjevac U, Gilic M et al. (2018) Mesoporous TiO₂ spheres as a photoanodic material in dye-sensitized solar cells. *Process Appl Ceram* 12:374–382. <https://doi.org/10.2298/PAC1804374T>.
 81. Xie F, Wang J, Li Y, Dou J, Wei M (2019) One-step synthesis of hierarchical SnO₂/TiO₂ composite hollow microspheres as an efficient scattering layer for dye-sensitized solar cells. *Electrochim Acta* 296:142–148. <https://doi.org/10.1016/j.electacta.2018.10.194>.
 82. Shalan AE, Rashad MM, Yu Y, Lira-Cantú M, Abdel-Mottaleb MSA (2013) Controlling the microstructure and properties of titania nanopowders for high efficiency dye sensitized solar cells. *Electrochim Acta* 89:469–478. <https://doi.org/10.1016/j.electacta.2012.11.091>.

83. Park K, Zhang Q, Myers D, Cao G (2013) Charge transport properties in TiO₂ network with different particle sizes for dye sensitized solar cells. *ACS Appl Mater Interfaces* 5:1044–1052. <https://doi.org/10.1021/am302781b>.
84. Yathisha RO, Arthoba Nayaka Y (2018) Structural, optical and electrical properties of zinc incorporated copper oxide nanoparticles: doping effect of Zn. *J Mater Sci* 53:678–691. <https://doi.org/10.1007/s10853-017-1496-5>.
85. Siraj K, Khaleeq-Ur-Rahman M, Hussain SI, Rafique MS, Anjum S (2011) Effect of deposition temperature on structural, surface, optical and magnetic properties of pulsed laser deposited Al-doped CdO thin films. *J Alloy Compd* 509:6756–6762. <https://doi.org/10.1016/j.jallcom.2011.03.183>.
86. Kharkwal D, Dhawan A (2024) Enhanced performance of dye-sensitized solar cells by mixing of metal-complex dyes. *J Electron Mater* 53:5334–5339. <https://doi.org/10.1007/s11664-024-11250-2>.
87. Toor RA, Sayyad MH, Nasr N, Sajjad S, Shah SAA, Manzoor T (2016) Efficiency enhancement of dye sensitized solar cells with a low cost co-adsorbant in N719 dye. *Int J Sustain Energy Environ Res* 5:46–50. <https://doi.org/10.18488/journal.13/2016.5.3/13.3.46.50>.
88. Nguyen PT, Lam BXT, Andersen AR, Hansen PE, Lund T (2011) Photovoltaic performance and characteristics of dye-sensitized solar cells prepared with the n719 thermal degradation products [Ru(LH)₂(NCS)(4- tert-butylpyridine)][N(Bu)₄] and [Ru(LH)₂(NCS)(1- methylbenzimidazole)][N(Bu)₄] *Eur J Inorg Chem* 2011:2533–2539. <https://doi.org/10.1002/ejic.201000935>.
89. Hočevár O, Berginc M, Topič M (2010) One Step Preparation of TiO₂ Layer for High Efficiency Dye-sensitized Solar Cell. *Acta Chim Slov* 57:405–409
90. Paramitha T, Munika DA, Saputra DR, (2024) Application of rice husk as a carbon source for substitution of sensitizer and counter electrode material in dye-sensitized solar cells. In: *Journal of Physics: Conference Series*. Institute of Physics.
91. Pujiarti H, Hidayat R, Wulandari P (2019) Enhanced efficiency in dye-sensitized solar cell by localized surface plasmon resonance effect of gold nanoparticles. *J Nonlinear Opt Phys Mater* 28. <https://doi.org/10.1142/S0218863519500401>.
92. Wanwong S, Sangkhun W, Wootthikanokkhan J (2018) The effect of co-sensitization methods between N719 and boron dipyrromethene triads on dye-sensitized solar cell performance. *RSC Adv* 8:9202–9210. <https://doi.org/10.1039/c8ra00862k>.
93. Arifin Z, Soeparman S, Widhiyanuriyawan D, Suyitno S (2017) Performance Enhancement of Dye-Sensitized Solar Cells Using a Natural Sensitizer. *Int J Photoenergy* 2017. <https://doi.org/10.1155/2017/2704864>.
94. Mensah-Darkwa K, Agyemang FO, Yeboah D, Akromah S (2021) Dye-sensitized solar cells based on graphene oxide and natural plant dye extract. In: *Materials Today: Proceedings*. Elsevier Ltd, pp 514–521.
95. Archana KM, Yogalakshmi D, Rajagopal R (2019) Application of green synthesized nanocrystalline CuI in the removal of aqueous Mn(VII) and Cr(VI) ions. *SN Appl Sci* 1. <https://doi.org/10.1007/s42452-019-0544-y>.
96. Akman E, Akin S, Ozturk T, Gulveren B, Sonmezoglu S (2020) Europium and terbium lanthanide ions co-doping in TiO₂ photoanode to synchronously improve light-harvesting and open-circuit voltage for high-efficiency dye-sensitized solar cells. *Sol Energy* 202:227–237. <https://doi.org/10.1016/j.solener.2020.03.108>.
97. Thulasi S, Arunprasad V, Karthik PS, Elatharasan G, Senthil P, Rajamanickam AT (2023) Design and Fabrication of High Performance Photoanode of Fe₂(MoO₄)₃/RGO Hybrid Composites for Triiodide Reduction in Dye-Sensitized Solar Cells. *J Clust Sci* 34:349–357. <https://doi.org/10.1007/s10876-021-02216-z>.
98. Teesetsopon P, Kumar S, Dutta J, Khoud A (2012) Photoelectrode Optimization of Zinc Oxide Nanoparticle Based Dye-Sensitized Solar Cell by Thermal Treatment. *Int J Electrochem Sci* 7:4988–4999
99. Lohar GM, Rupnawar D V, Shejawal R V, Fulari A V (2034) Preparation of natural dyes from salvia and spathodea for TiO₂-based dye-sensitized solar cells (DSSCs) and their electrochemical impedance spectroscopic study under light and dark conditions. <https://doi.org/10.1007/s12034-020-02180-w>.
100. Ezema CG, Nwanya AC, Ezema BE, Patil BH, Bulakhe RN, Ukoha PO et al. (2016) Photo-electrochemical studies of chemically deposited nanocrystalline meso-porous n-type TiO₂ thin films for dye-sensitized solar cell (DSSC) using simple synthesized azo dye. *Appl Phys A Mater Sci Process* 122:435. <https://doi.org/10.1007/s00339-016-9965-2>.