



Exploring the impact of metal doping and alternative electrodes on the performance of dye-sensitized solar cells

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ABSTRACT

This study explores the synthesis and characterization of metal-doped TiO₂ thin films for applications in dye-sensitized solar cells (DSSCs). Titanium dioxide (TiO₂) films were doped with various metal ions such as Ag⁺, Zn²⁺, Fe³⁺, and Co²⁺, to enhance the photoelectrochemical properties of the photoanode. The films were characterized using various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–Vis spectroscopy, and X-ray photoelectron spectroscopy (XPS). The doping process was found to influence the morphology, surface area, and optical properties of the TiO₂ films, resulting in enhanced light absorption, particularly in the visible range. The effects of metal doping on the performance of the DSSCs were evaluated, showing that Co²⁺ and Ag⁺ doping resulted in improved efficiency compared to undoped TiO₂, with the Co²⁺-doped TiO₂ achieving the highest power conversion efficiency of 2.85%. Additionally, the incorporation of reduced graphene oxide (rGO) as a counter electrode demonstrated a significant enhancement in DSSC performance, even surpassing traditional platinum-based counter electrodes. The results suggest that metal doping and rGO incorporation offer promising strategies for improving DSSC efficiency. This study highlights the potential of metal-doped TiO₂ photoanodes and rGO counter electrodes in advancing the development of cost-effective, high-performance DSSCs for sustainable solar energy applications.

1 Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant attention as alternative photovoltaic technologies due to the growing demand for sustainable energy solutions. Compared to conventional silicon-based

solar cells, DSSCs offer advantages, such as lower fabrication cost, simple processing methods, and structural versatility. Since the pioneering work of O'Regan and Grätzel, DSSCs have been considered promising candidates to complement traditional p–n junction photovoltaic devices [1–7].

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DSSCs are a type of solar cell consisting of a photoanode (working electrode, WE) sensitized with specialized dyes to convert solar energy more efficiently, an electrolyte, and a photocathode (counter electrode, CE). The WE acts as the electron acceptor, while the dye functions as the electron donor. The electrolyte supports the redox reactions, and the CE serves as the catalyst in this process [8]. The energy efficiency of DSSCs depends on the light absorption capacity, the transport and injection of photogenerated charge carriers, and the balance between charge collection and recombination. The morphology and structure of the WE play a crucial role in determining these parameters [9]. As a WE, TiO_2 stands out more significantly compared to other semiconductor metal oxides (such as ZnO , Fe_2O_3 , CeO_2 , SrTiO_3 , etc.). This is because TiO_2 offers advantages such as fast electron collection and a high charge transport rate as an anode base material [10]. In recent years, efforts have been made to improve the charge transport capability, high diffusion rate, and large surface area of the TiO_2 nanostructure for the development of high-performance DSSCs. An effective strategy for modifying the electronic properties of TiO_2 is the use of dopants [11].

Various studies have focused on improving the optical and electrical properties of TiO_2 WEs through doping with transition metal ions such as Ag, Fe, Ni, and Cd [11–15]. These studies have shown that doping prevents the growth of TiO_2 nanoparticles, leading to the formation of smaller particles. Consequently, the resulting increase in surface area, which allows for greater dye loading, has been observed to enhance both light absorption and current density. Noble metals like Ag^+ act as electron traps at the TiO_2 interface, forming Schottky barriers that suppress charge recombination and increase electron lifetime [16]. Zn^{2+} doping improves crystallinity and electron mobility due to its ionic radius compatible with Ti^{4+} . Transition metal ions like Fe^{3+} broaden light absorption toward the visible region by forming intermediate energy levels within the TiO_2 band structure, while Co^{2+} doping has been reported to improve interfacial charge transfer processes in DSSCs [17].

The dye used in DSSCs plays a critical role in absorbing solar radiation and enhancing the efficiency of the cell. Ruthenium (Ru) polypyridyl complexes (N3, N719) developed by the Grätzel group stand out

as suitable sensitizers in terms of efficiency and stability. However, the high cost of these dyes has led to a search for more affordable alternatives. Environmentally friendly and cost-effective dyes can be obtained by extracting them from fruits, roots, leaves, and flowers. Dyes containing anthocyanins are frequently preferred in DSSCs because their structures contain carboxyl and hydroxyl groups, allowing them to adhere strongly to TiO_2 [18, 19]. In the study by Ramelon et al. (2016), anthocyanin extracted from hibiscus was used as a photosensitizer in DSSCs based on nanostructured TiO_2 . In that study, the nanostructured TiO_2 powder was calcined at 600°C and then prepared using the sol–gel method. TiO_2 was produced in several different thicknesses. The results showed that the sample with a TiO_2 layer thickness of $4.75 \pm 0.8 \mu\text{m}$ exhibited the highest efficiency. The reported values were $I_{\text{sc}} = 0.000080 \text{ A}$, $V_{\text{oc}} = 0.389463 \text{ V}$, $\text{FF} = 0.335$, and $\eta = 3.0 \times 10^{-3}\%$. Consequently, it was observed that increasing the layer thickness did not significantly enhance the anthocyanin absorption [20]. Based on this information, the present study uses N719 dye as the primary sensitizer, while dye obtained from hibiscus leaves is used to compare cell performance.

In recent years, platinum (Pt) has been widely preferred as the CE in DSSCs due to its high electrical conductivity, superior catalytic properties, and low charge transfer resistance (R_{ct}). However, due to the high cost of Pt, alternative materials have been sought for the cell. Graphene is a next-generation carbon-based material with a two-dimensional structure. It exhibits superior electrical, thermal, and mechanical properties. It possesses a remarkably large surface area of $500\text{--}1200 \text{ m}^2/\text{g}$ and a conductivity of approximately $1000\text{--}1500 \text{ S/m}$. Reduced graphene oxide (rGO) is a carbon material with properties similar to graphene, obtained by reducing graphene oxide (GO) through chemical, thermal, or electrochemical methods. During this reduction process, the oxygen-containing functional groups on the GO surface are partially or completely removed, resulting in a more conductive structure [8]. In the study by Qui et al. (2014), rGO was synthesized for the CE in DSSCs using prepared using the drop-casting method followed by thermal treatment. The as-prepared rGO CEs were named rGO, rGO-0.1, rGO-0.2, and rGO-0.3 based on the amount of hydrazine hydrate used. The efficiency (η) of DSSCs based on rGO CE containing 0.3 mg hydrazine

hydrate (2.62%) was 43.2% higher than those with rGO CEs without hydrazine hydrate (1.83%). Although the performance of DSSCs based on rGO CE was still lower than those using Pt CEs, it was suggested that graphene has great potential as a CE in DSSCs due to its excellent electrical conductivity, unique crystalline structure, and chemical stability [21]. rGO stands out as an important material for CE applications and has the potential to enhance electron transfer efficiency. By reducing GO, oxygen bonds create sp³ hybridization on rGO, furthermore, due to the higher electronegativity of oxygen atoms compared to carbon atoms, rGO becomes a doped semiconductor, where the charge flow is influenced by negatively charged oxygen atoms and the positively charged carbon network. There are many studies in the literature where GO and rGO are used as the CE in DSSCs [22–26]. These innovative components are of great importance for increasing the efficiency of DSSCs technology and providing an environmentally friendly alternative to modern energy needs.

In this study, metal ions (Ag^+ , Zn^{2+} , Fe^{3+} , Co^{2+}) were doped into TiO_2 , which was synthesized via the sol–gel method, at varying concentrations. As an alternative to the widely used N719 dye, a natural dye extracted from hibiscus flowers was employed as a sensitizer for the solar cell. The CEs were prepared using GO and rGO, both synthesized via the Hummers method. These materials were then applied to fluorine-doped tin oxide (FTO) conductive substrates using the doctor-blade technique. The resulting DSSCs were subsequently assembled for performance evaluation. Although many studies have been conducted on single metal-doped TiO_2 photoanodes for DSSCs, there are few studies that directly compare different metal ion percentages under the same conditions. Evaluating these photoanodes in conjunction with rGO counter electrodes and various sensitizers provides a comprehensive overview of material interactions in DSSCs.

2 Experimental section

The materials used in this study, the synthesis procedures of the working electrode by the sol–gel method, the synthesis procedure of GO and rGO, as well as the preparation of the CE, the preparation of the electrolyte, and both the N719 and hibiscus dyes, along with the characterizations performed are provided in detail in the Supporting Information section.

3 Results and discussion

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

The SEM and EDS spectra of the working electrodes, synthesized via the sol–gel method with P25 applied onto the FTO substrate using the doctor-blade technique, are shown in Fig. S1 of the Supporting Information. SEM analyses presented in Fig. S2 and Fig. S3 of the Supporting Information were used to examine the surface morphologies of GO-PVP and rGO-PVP structures, synthesized by the Hummers method and applied to the FTO substrate using the ‘Doctor Blade’ technique, on the CE of DSSCs. EDS analysis of the GO-PVP and rGO-PVP photocathodes was performed to determine the surface elemental composition and to verify the absence of impurities in the structure. It is shown in the Supporting Information Fig. S4.

3.2 X-ray photoelectron spectroscopy (XPS) analysis

XPS analysis was carried out and Supporting Information (Figures S5, S6, S7, S8, S9, S10, S11, S12, S13, S14, S15) is provided to determine the chemical composition and valence states of the elements of undoped and different percentages (Ag^{1+} , Zn^{2+} , Fe^{3+} , Co^{2+})-doped TiO_2 photoanode electrodes synthesized by the sol–gel method and GO-PVP and rGO-PVP photocathode electrodes synthesized by the Hummers method. Additionally, XPS analyses for the GO-PVP and rGO-PVP used as DSSC photocathodes are presented in the Supporting Information Fig. S16.

3.3 X-ray diffraction (XRD) analysis

XRD analysis was performed to determine the phases, crystalline phases, structures, and grain sizes of undoped and metal-doped (Ag^{1+} , Zn^{2+} , Fe^{3+} , Co^{2+}) TiO_2 films produced by the sol–gel method as well as GO-PVP and rGO-PVP samples synthesized by the Hummers method. The XRD patterns of the films synthesized by the sol–gel method (undoped TiO_2 and TiO_2

doped with metal ions such as Ag^{1+} , Zn^{2+} , Fe^{3+} , Co^{2+}) and FTO, GO-PVP/FTO and rGO-PVP /FTO films are provided in the Supporting Information (Figures S17, S18, S19, S20, S21).

3.4 Brunauer–emmett–teller (BET) analysis

The BET surface area and pore size distribution of undoped TiO_2 and 1.0 M Ag^{1+} , Zn^{2+} , Fe^{3+} , and Co^{2+} -doped TiO_2 used in the working electrodes of the DSSCs were investigated via N_2 adsorption–desorption isotherms. BET analysis was performed to determine how doping changes the surface area and pore size. The N_2 adsorption–desorption isotherms and the

BJH pore size distributions of the working electrodes (undoped TiO_2 and TiO_2 doped with metal ions such as Ag^{1+} , Zn^{2+} , Fe^{3+} , Co^{2+}) are given in Figs. 1, 2, 3, 4, 5.

The pore size distribution curves were calculated using the Barrett–Joyner–Halenda (BJH) method. Among the six different types of nitrogen adsorption/desorption isotherms, the isotherms of the photoanodes align with the Type IV, exhibiting H2-type hysteresis loops. This type of isotherm indicates the presence of mesopores in the structure. The resulting mesoporous structure is suitable for the diffusion and transport of the electrolyte during the electrochemical reaction process [27]. The presence of H2 hysteresis is generally associated with ink-bottle type pores

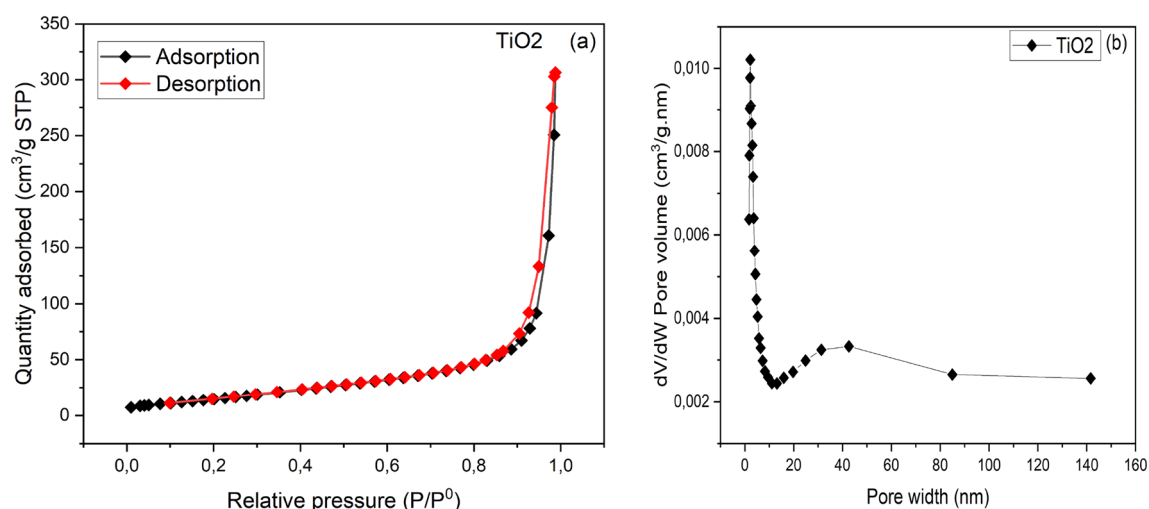


Fig. 1 Pure TiO_2 . **a** N_2 adsorption–desorption isotherms; **b** BJH pore size distribution

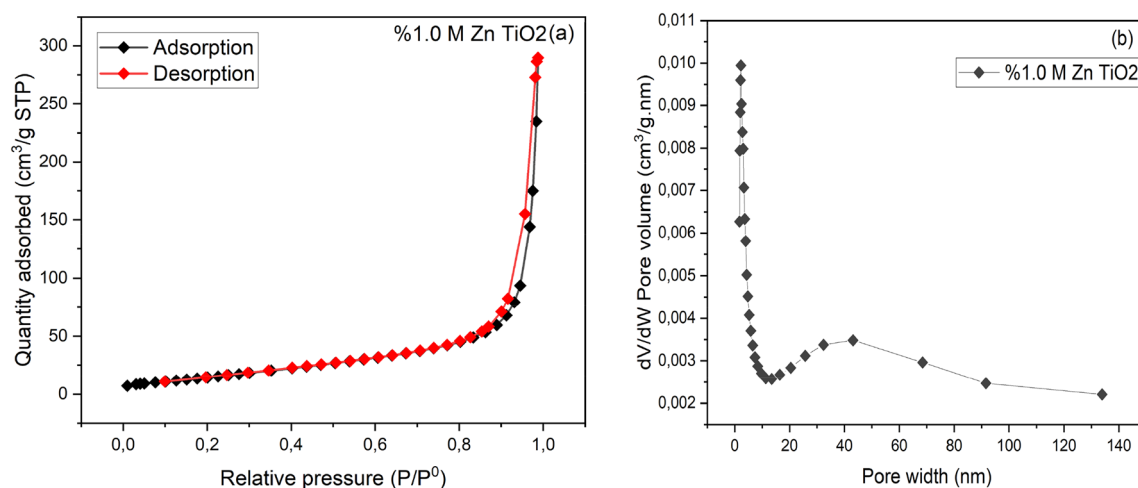


Fig. 2 1.0% M Zn^{2+} TiO_2 . **a** N_2 adsorption–desorption isotherms; **b** BJH pore size distribution

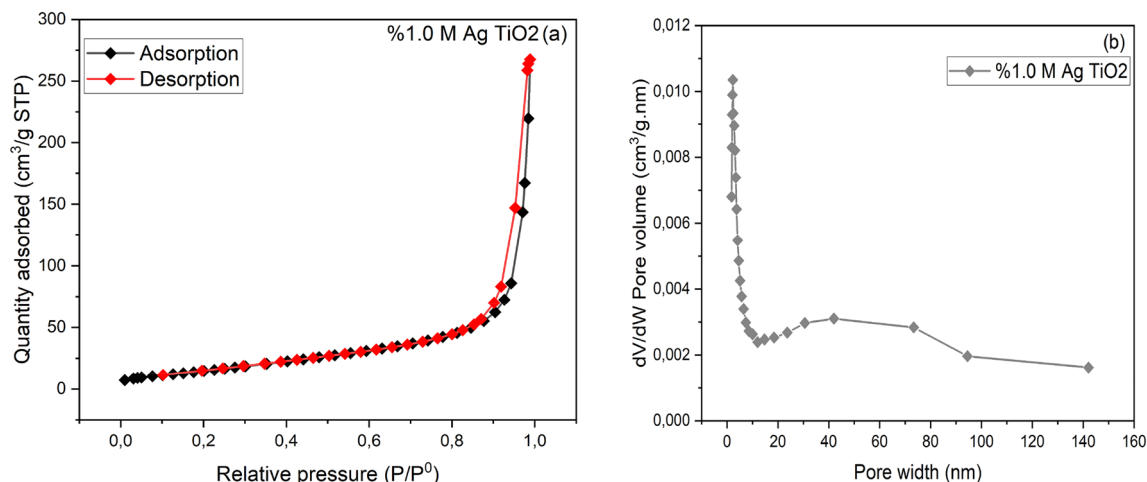


Fig. 3 1.0 M Ag⁺ TiO₂. **a** N₂ adsorption–desorption isotherms; **b** BJH pore size distribution

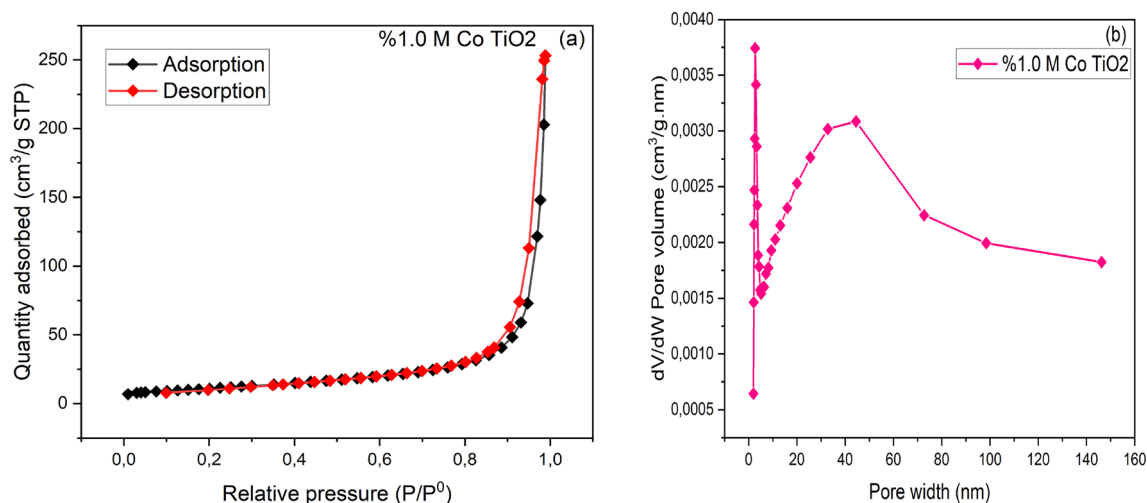


Fig. 4 1.0% M Co²⁺ TiO₂. **a** N₂ adsorption–desorption[isotherms. **b** BJH pore size distribution

consisting of narrow necks and wider pore bodies. In this study, the H2-type hysteresis may originate from the aggregation of TiO₂ nanoparticles, leading to a disordered mesoporous network. Although metal ion incorporation may slightly modify the pore structure, the overall mesoporous framework remains preserved, and no significant pore collapse is observed after doping. TiO₂ nanostructures with large surface area and narrow pore size distribution help in more dye loading and more efficient electrolyte infiltration when used as a photoanode in DSSC. These are two important factors that will help in improving charge transport and hence increasing the power conversion efficiency in DSSC [28]. The high surface area can provide more

sites for dye adsorption, while the fast photoelectron transfer channel enhances the photogenerated electron transfer to complete the circuit [29]. It shows that when the specific surface area of TiO₂ increases with doping, the dispersion of the doping on the TiO₂ surface and the photocatalytic and adsorption active sites are improved.

The effect of the surface area and particle size of TiO₂ on charge transport properties has been well established in the literature. Confirm in the correct order. Therefore, the electron transport with the TiO₂ network changes with the effect of particle size on the mean free path. A larger particle size provides both a longer travel distance and a lower collision

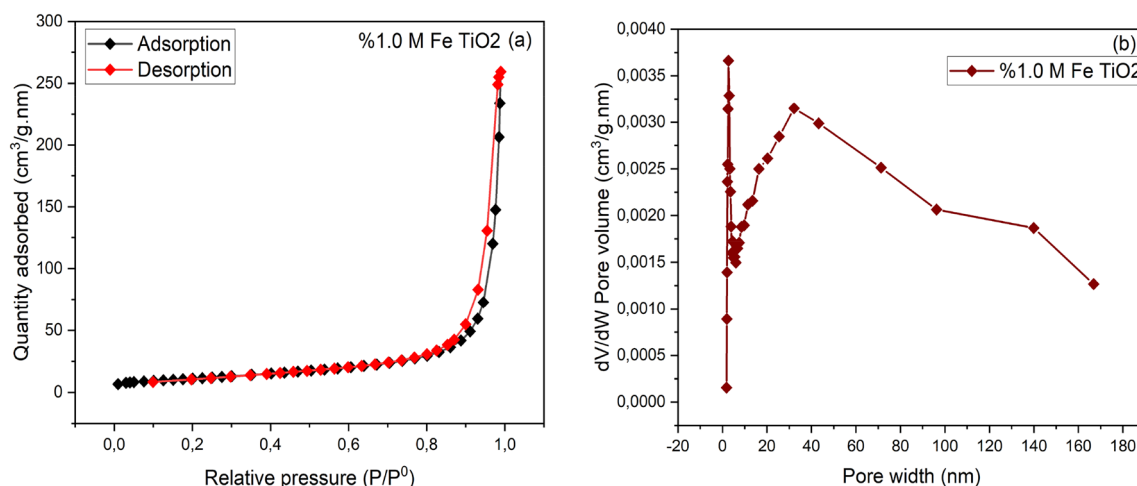


Fig. 5 1.0% M Fe³⁺ TiO₂. **a** N₂ adsorption–desorption isotherms. **b** BJH pore size distribution

probability. In addition, the surface area has a strong effect on recombination when in contact with the electrolyte. Accordingly, large TiO₂ particles with high recombination resistance, low transport resistance, and low chemical capacitance should exhibit the longest diffusion length and, consequently, higher efficiency. It is evident that in the TiO₂ nanoparticle working electrode, there should be a balance between the morphological factors of TiO₂, which determine the light-harvesting ability of the entire network, and the charge collection efficiency driven by the particle size [30]. The structural properties of the working electrodes (undoped TiO₂ and TiO₂ doped with metal ions such as Ag¹⁺, Zn²⁺, Fe³⁺, Co²⁺), obtained from the BET analysis are summarized in Table 1. The average pore size of Zn²⁺ and Fe³⁺-doped TiO₂ samples increased significantly compared to pure TiO₂ due to the influence of dopant ions on nanoparticle growth and packing. Zn²⁺ doping produces larger particles with less dense packing, while Fe³⁺ doping results in irregular aggregation of smaller particles, both leading to broader pore size distributions. Although larger pores can enhance electrolyte penetration, the heterogeneous

pore network may impede uniform diffusion, contributing to the reduced DSSC performance observed for these samples. For the Fe³⁺-doped sample, despite the smaller particle size, the irregular aggregation leads to an increase in average pore size.

Among the DSSCs, TiO₂ doped with 1.0% Co²⁺ had the highest BET surface area (73.82 m²/g) and medium pore size (~ 22 nm); this was associated with the highest photocurrent ($J_{sc} = 13.8$ mA/cm²) and PCE ($\eta = 2.85\%$) among Co²⁺-doped cells. In contrast, TiO₂ doped with 1.0% Zn²⁺ had a lower surface area (36.79 m²/g) and larger particle size (~ 163 nm); this led to a reduction in dye adsorption sites and consequently lower efficiency ($\eta = 0.48\%$). Interestingly, while TiO₂ doped with 1.5% Co²⁺ and Ag⁺ showed slightly higher J_{sc} values, their PCEs did not increase proportionally due to increased charge recombination and microstress effects caused by higher dopant concentrations; this highlights that surface area alone does not guarantee higher efficiency. These observations emphasize that optimum DSSC performance requires a balance between surface area, pore structure, and electronic

Table 1 Structural properties of pure TiO₂ and 1.0% M (Ag¹⁺, Zn²⁺, Fe³⁺, Co²⁺)-doped TiO₂ WE according to BET analysis

WE	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 Zn TiO ₂	36.79	163.09	0.390	0.390	35.88	30.38
1.0% M Ag TiO ₂	60.15	99.75	0.473	0.474	24.63	23.83
1% M Co TiO ₂	73.82	81.28	0.528	0.530	22.24	21.24
1.0% M Fe TiO ₂	36.07	54.01	0.400	0.400	36.38	31.48

properties, rather than relying solely on BET surface area.

3.5 Raman analysis

Before the application of the doctor-blade technique onto FTO, 1.0% PVP was added to the GO structure synthesized by the Hummers method during the synthesis phase. Figure 6 shows the Raman spectra of the GO-PVP and rGO-PVP used as photocathodes in the DSSCs.

The D vibration band formed by the breathing mode of j point photons having A_{1g} symmetry is observed at 1348.30 and 1356.40 cm^{-1} for GO-PVP and rGO-PVP, respectively. In addition, the G

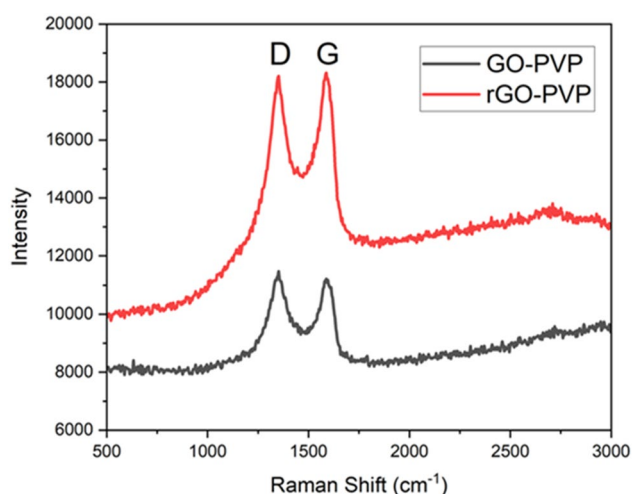


Fig. 6 Raman spectra of GO-PVP and rGO-PVP used in the photocathode in DSSCs

vibration band obtained from the first-order scattering of E_{2g} phonons by sp^2 carbon was detected at 1592.02 for GO and 1584.15 cm^{-1} for rGO-PVP. The ratio of D band and G band peak intensities was determined to detect the structural disorder of GO-PVP and rGO-PVP. While the I_D/I_G ratio was found to be 1.03 for GO-PVP, it was found to be 0.97 for rGO-PVP. The results are consistent with the literature [31, 32]. The reason for the lower I_D/I_G in rGO-PVP is attributed to an increase in the in-plane sp^2 conjugated carbon lattice due to the addition of PVP nanoparticles. The intensity difference between the D and G peaks in rGO-PVP is less than that of GO-PVP, which is attributed to the removal of oxygen groups from GO during the reduction process and the restoration of the graphene lattice structure [33]. The decrease in the I_D/I_G ratio from GO-PVP to rGO-PVP indicates a partial restoration of the sp^2 carbon network during the reduction process, suggesting some defect healing. This structural rearrangement leads to improved graphitic ordering, although some defects remain. Furthermore, slight shifts observed in the D and G bands may be attributed to interactions between PVP molecules and the graphene surface, which can modify the local electronic environment and influence Raman peak positions.

3.6 UV-visible spectrophotometer measurements and optical analysis

Absorption measurements of undoped TiO_2 and metal-doped TiO_2 thin films synthesized by the sol-gel method are shown in Figs. 7, 8, 9, 10, 11 by

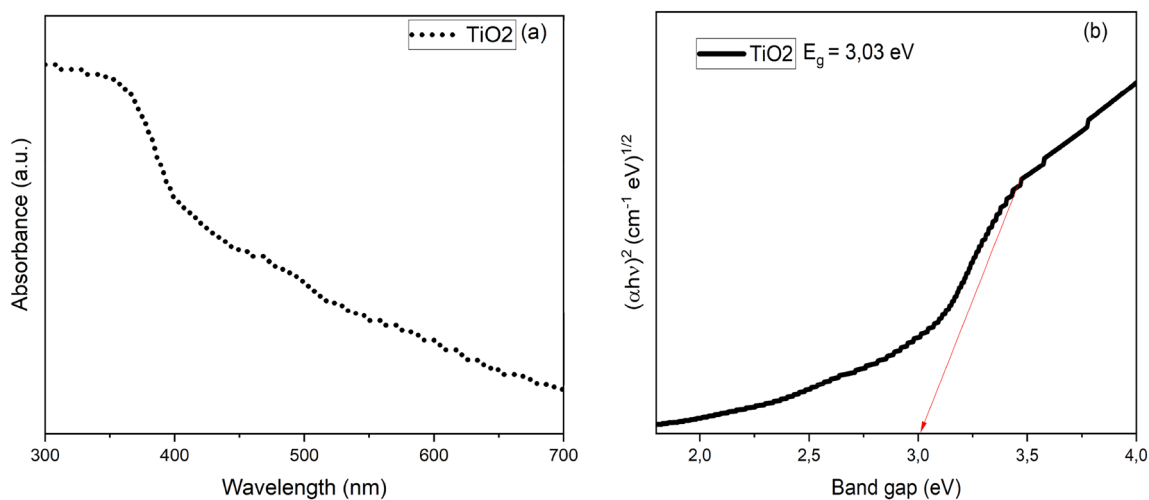


Fig. 7 Absorption **a** and optical band gap **b** graphs of pure TiO_2 photoanode film synthesized by the sol-gel method

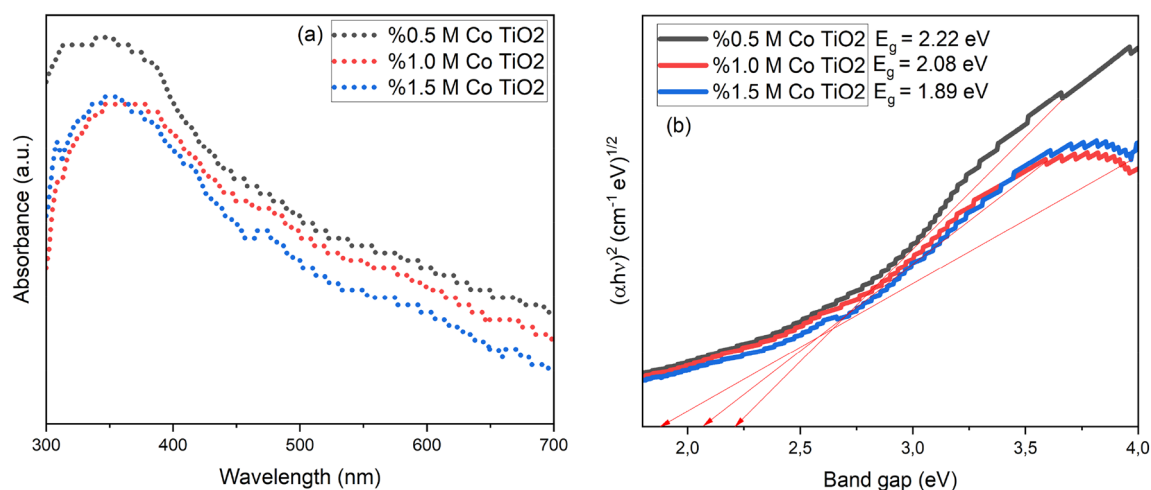


Fig. 8 Absorption **a** and optical band gap **b** graphs of TiO₂ photoanode film doped with (0.5, 1.0, and 1.5 M Co²⁺) synthesized by the sol–gel method

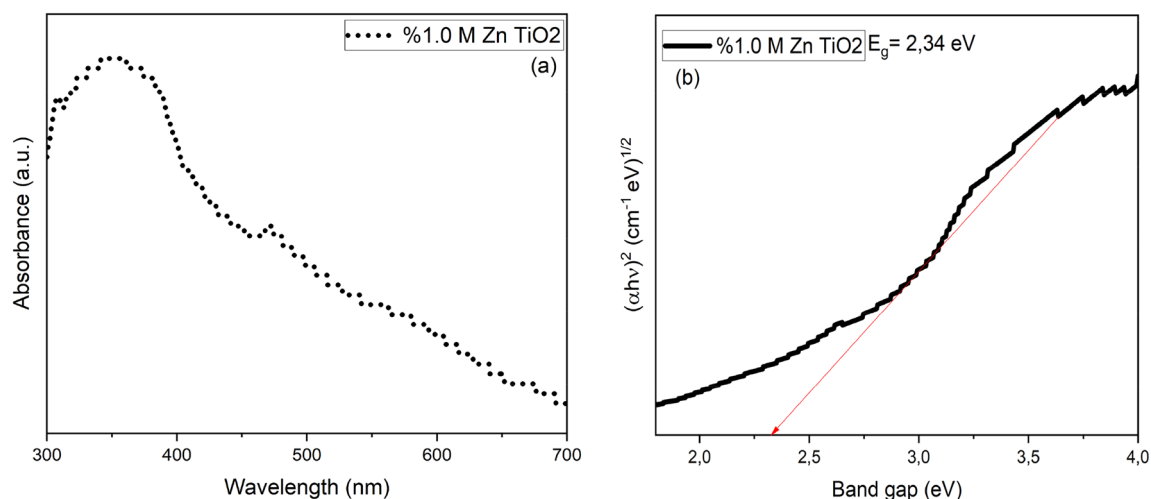


Fig. 9 Absorption **a** and optical band gap **b** graphs of 1.0% M Zn²⁺-doped TiO₂ photoanode film synthesized by the sol–gel method

evaluating the determination of optical properties in the ultraviolet (UV) and visible regions in the range of 300–700 nm.

The graphs indicate that doping significantly alters the absorption properties. Additionally, the change in the band gap energy upon doping TiO₂ was determined using the $(\alpha h\nu)^2$ –band gap (photon energy–eV) plot. The band gap (E_g) of undoped pure and doped TiO₂ thin films was calculated using the Tauc equation, as summarized in Table 2. It is clearly observed in the spectra that the absorption of undoped and doped TiO₂ is higher in the UV region and lower in the visible region. The energy gap of the materials varies according to the crystal defects formed by the dopant. In

addition, it is affected by many factors such as particle size, impurity centers, micro-strain, light absorption of the material, oxygen vacancies, displacement density and film thickness. These results show that E_g values decrease with the increase in the amount of doping on the same element. This decrease in E_g values causes the optical properties to improve by providing more photon absorption. At the same time, this decrease indicates that low energy photons are also absorbed for photoreaction. Nanoscale size changes directly affect the optical properties. The quantum confinement effect occurring at small sizes provides the formation of lower levels in the energy range of the prepared films and these levels cause separation. Therefore,

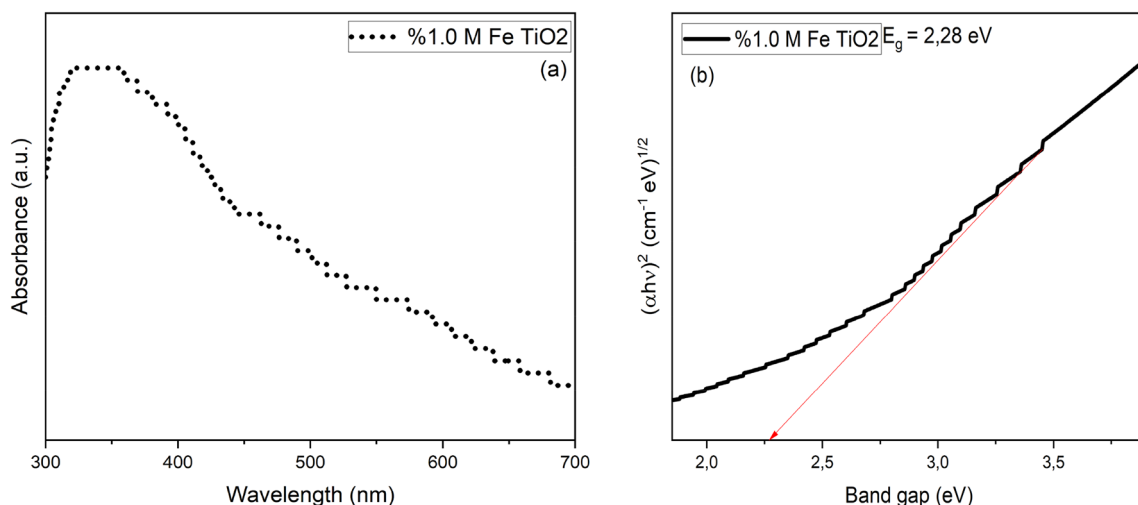


Fig. 10 Absorption **a** and optical band gap **(b)** graphs of a 1.0% M Fe³⁺-doped TiO₂ photoanode film synthesized by the sol–gel method

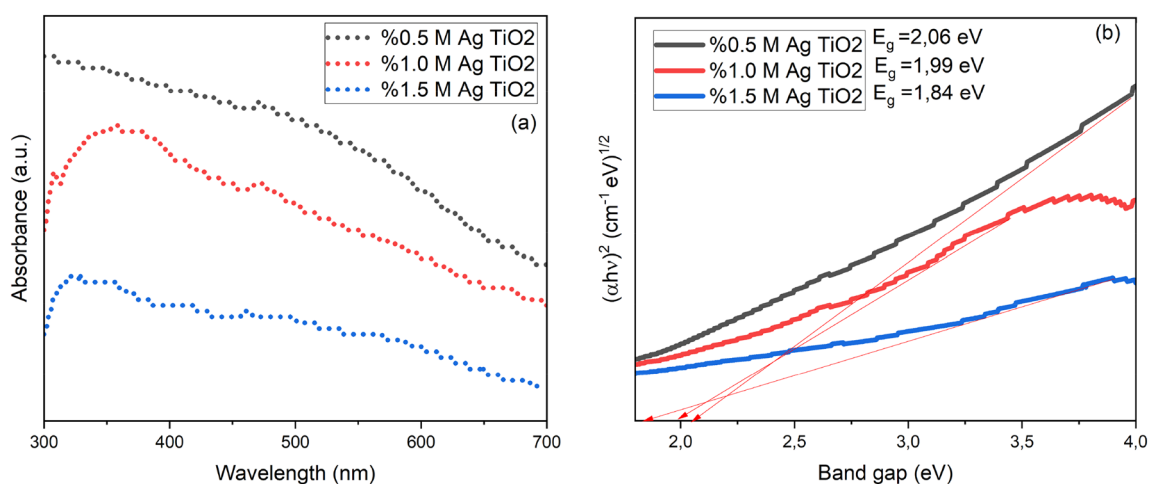


Fig. 11 Absorption **a** and optical band gap **b** graphs of TiO₂ photoanode film doped with (0.5, 1.0, and 1.5% M Ag¹⁺) synthesized by the sol–gel method

Table 2 Determination of band gap values of photoanode electrodes

Photoanode electrodes	Band gap (eV)
TiO ₂	3.03
0.5% M Co ²⁺ TiO ₂	2.22
1.0% M Co ²⁺ TiO ₂	2.08
1.5% M Co ²⁺ TiO ₂	1.98
1.0% M Zn ²⁺ TiO ₂	2.34
1.0% M Fe ³⁺ TiO ₂	2.28
0.5% M Ag ¹⁺ TiO ₂	2.06
1.0% M Ag ¹⁺ TiO ₂	1.99
1.5% M Ag ¹⁺ TiO ₂	1.84

changing sizes have caused different band gap values [34, 35]. Different metal dopants (Co²⁺, Zn²⁺, Fe³⁺, Ag⁺) affect the TiO₂ band structure differently, leading to the observed variations in band gap values. The band gap reduction is attributed to the formation of dopant-induced localized states within the TiO₂ lattice. TiO₂ was considered as a direct band gap semiconductor in the Tauc plot analysis. Moderate metal doping, such as 1.0% Co in TiO₂-N-rGO, enhances light absorption and electron transport, which increases the J_{sc} and overall PCE. In contrast, higher doping levels lead to increased defect-induced recombination, resulting in a lower FF and reduced efficiency, despite further narrowing of the band gap. These observations highlight

Table 3 Performance results of DSSCs using pure TiO₂ as the photoanode

Cell code	V_{OC} (V)	J_{SC} (mA/cm ²)	P_{MAX}	FF	PCE (η) (%)
TiO ₂ -N-GO	0.71	6.06	0.17	0.39	0.85
TiO ₂ -H-GO	0.57	0.57	0.03	0.76	0.13
TiO ₂ -N-rGO	0.69	8.39	0.3	0.51	1.5
TiO ₂ -H-rGO	0.56	0.95	0.03	0.55	0.15

that band gap reduction alone does not ensure higher DSSC performance; the dopant concentration must be optimized to balance light absorption enhancement and recombination suppression. The I - V results in Table 4 confirm this behavior.

3.7 Spectrophotometric analysis of dyes

Spectrophotometric analysis of the liquid forms of the N719 sensitizers and the natural sensitizer extracted from the hibiscus plant. The optical absorption spectra of the samples were measured and are presented in the Supporting Information Fig. S22a and b.

3.8 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis was performed to analyze the bonding structure of the liquid forms of the N719 sensitizers and the natural dye extracted from the hibiscus plant. Variable wavelengths were obtained showing various functional bonds which can be seen in Supporting Information Fig. S23a and b.

3.9 Calculation of photovoltaic parameters of DSSCs

The I - V measurements of the DSSCs were performed using the Keithley 2400 Sourcemeter. The current values were recorded at specific voltage intervals under AM 1.5G standard illumination (100 mW/cm²) at room temperature using a HelioSim CL60 solar simulator.

To investigate the effect of TiCl₄ treatment on cells with power conversion efficiencies above 1.0%, a 0.05 M TiCl₄ solution was applied to the cleaned FTO base material and kept at 70 °C for 50 min. Then, the pastes synthesized with sol-gel were applied using the doctor-blade method and calcined at 500 °C for 1 h.

According to the results presented in Table 3, the use of rGO instead of GO in the photocathode provided higher current density (J_{SC}), and thus higher power conversion efficiency. The efficiency obtained from the hibiscus plant was weak compared to N719. This can be attributed to differences in dye loading, binding strength, and stability. N719 dye contains carboxylate linker groups that form strong chemical bonds with the TiO₂ surface, resulting in efficient electron injection and stable dye adsorption [36, 37]. In contrast, hibiscus dye consists primarily of anthocyanin molecules that interact with TiO₂ through weaker physical adsorption, resulting in lower dye loading and reduced electron transfer efficiency. Furthermore, natural dyes generally exhibit lower photochemical stability and are more susceptible to desorption and degradation in the electrolyte medium [38]. Table 4 shows the performances of DSSCs with different percentages of metal element doping. While a significant increase in the Co²⁺ and Ag¹⁺-doped photoanodes obtained from DSSCs formed with 0.5, 1.0

Table 4 Performance results of DSSCs using different percentages of metal-doped TiO₂ in the photoanode

Cell code	V_{OC} (V)	J_{SC} (mA/cm ²)	P_{MAX}	FF	PCE (η) (%)
0.5 Co TiO ₂ -N-rGO	0.78	11.3	0.34	0.38	1.70
1.0 Co TiO ₂ -N-rGO	0.77	13.8	0.56	0.53	2.85
1.5 Co TiO ₂ -N-rGO	0.72	13.3	0.4	0.41	2.01
1.0 Co TiO ₂ -H-rGO	0.58	0.54	0.025	0.80	0.13
0.5 Ag TiO ₂ -N-rGO	0.73	12.5	0.41	0.45	2.08
1.0 Ag TiO ₂ -N-rGO	0.71	12.2	0.44	0.51	2.24
1.5 Ag TiO ₂ -N-rGO	0.79	14.0	0.46	0.42	2.36
1.0 Ag TiO ₂ -H-rGO	0.6	0.59	0.024	0.66	0.12
1.0 Zn TiO ₂ -N-rGO	0.73	1.5	0.093	0.84	0.48
1.0 Zn TiO ₂ -H-rGO	0.57	0.42	0.02	0.63	0.08
1.0 Fe TiO ₂ -N-rGO	0.74	1.73	0.1	0.76	0.49
1.0 Fe TiO ₂ -H-rGO	0.56	0.12	0.007	0.95	0.034

and 1.5% M Co²⁺, Ag¹⁺, Zn²⁺, Fe³⁺-doped TiO₂ thin films is observed compared to pure TiO₂, the Co²⁺ and Ag¹⁺-doped photoanodes are less efficient compared to pure TiO₂. When the doping ratio for Co²⁺ and Ag¹⁺ was increased from 1.0 to 1.5%, a decrease in the efficiency value occurred. This decrease can be attributed to the formation of defect sites by excess dopant ions, enhancing charge recombination and hindering electron mobility; this is consistent with previous studies on metal-doped TiO₂ DSSCs [39, 40]. Although Zn²⁺ and Fe³⁺ doping resulted in a slight narrowing of the band gap, the J_{SC} values decreased significantly. This indicates that band gap reduction alone does not necessarily lead to higher photocurrent in DSSCs. The lower J_{SC} values may be attributed to increased charge recombination and trap states introduced by dopant ions, which can hinder efficient electron transport within the TiO₂ photoanode. In addition, differences in sensitizer type also play an important role; natural dyes such as hibiscus generally exhibit lower electron injection efficiency compared to ruthenium-based dyes like N719, which can further contribute to reduced photocurrent density. Among the metal element-doped DSSCs, the 1.0 Co TiO₂-N-rGO cell exhibited the best performance with 2.85% efficiency. In the TiO₂-N-GO cell, it was found to be relatively low with 0.39 FF, and the 0.5 Co TiO₂-N-rGO cell had 0.38 FF. Therefore, this indicates that there is a significant resistance in the cell or the mobility of the carriers is low. When the lower efficiency of GO compared to rGO was obtained in the CE, it was decided to use rGO as the CE material in the prepared cells. While the efficiency of the TiO₂-N-GO cell was 0.85%, the efficiency of the TiO₂-N-rGO cell was 76% higher with 1.5%. Because GO has semiconductor properties close to insulators, rGO has high conductivity. In addition, the specific surface area of rGO is higher compared to GO (Figs. 12, 13, 14, 15, 16, 17, 18).

To improve interparticle coupling, increase the effective surface area, and reduce charge recombination at the TiO₂/electrolyte interface, a TiCl₄ treatment was applied to the TiO₂ photoanode; this can enhance electron transport and improve the overall performance of DSSCs. TiCl₄ concentration is also one of the important parameters on the performance results of DSSCs. The performance results of DSSCs treated with TiCl₄ are shown in Table 5. While a positive effect was observed in the performance of TiCl₄-treated cells in some cells, a decrease was observed in some. The effect of TiCl₄ surface

treatment showed different trends depending on the photoanode composition. For pristine TiO₂ photoanodes, TiCl₄ treatment improved device performance, increasing PCE from 0.85 to 1.22% for N719-sensitized cells. This improvement can be attributed to surface defect passivation, improved interparticle connectivity, and enhanced electron transport pathways. However, in metal-doped TiO₂ photoanodes, a decrease in efficiency was observed after TiCl₄ treatment. For example, the efficiency of 1.0% Co-doped TiO₂ decreased from 2.85 to 2.23%, while Ag-doped TiO₂ showed a more pronounced reduction. This behavior may result from excessive surface modification, where the additional TiO₂ layer partially covers dopant-active sites, alters pore accessibility, and increases charge recombination. These findings indicate that the effectiveness of TiCl₄ treatment strongly depends on the initial electronic structure and surface condition of the photoanode.

Table 6 shows the performance results of DSSCs using Pt in the photocathode. The efficiency of the cell using rGO in the photocathode is the same as the efficiency of the cell using Pt, which is 1.5%. This situation can be explained by the fact that rGO is more conductive than graphene oxide. rGO has good electronic transport properties and a high surface/volume ratio [41].

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

IPCE, which measures the number of electrons produced by a solar cell according to the number of photons reaching its active surface under monochromatic light in the UV and visible regions (300–700 nm), provides important information about the performance of the DSSC.

The DSSC coded as S-H-GO absorbs light in the 300–400 nm range, with its peak efficiency of 4.04% occurring at 349 nm. In comparison, the S-N-GO cell shows a higher efficiency of 5.4% at 330 nm. As shown in Fig. 19, the DSSC coded as S-H-rGO also absorbs in the 300–400 nm range, with a peak efficiency of 4.09% at 350 nm. Meanwhile, the S-N-rGO cell demonstrates the highest efficiency of 6.15% at 334 nm.

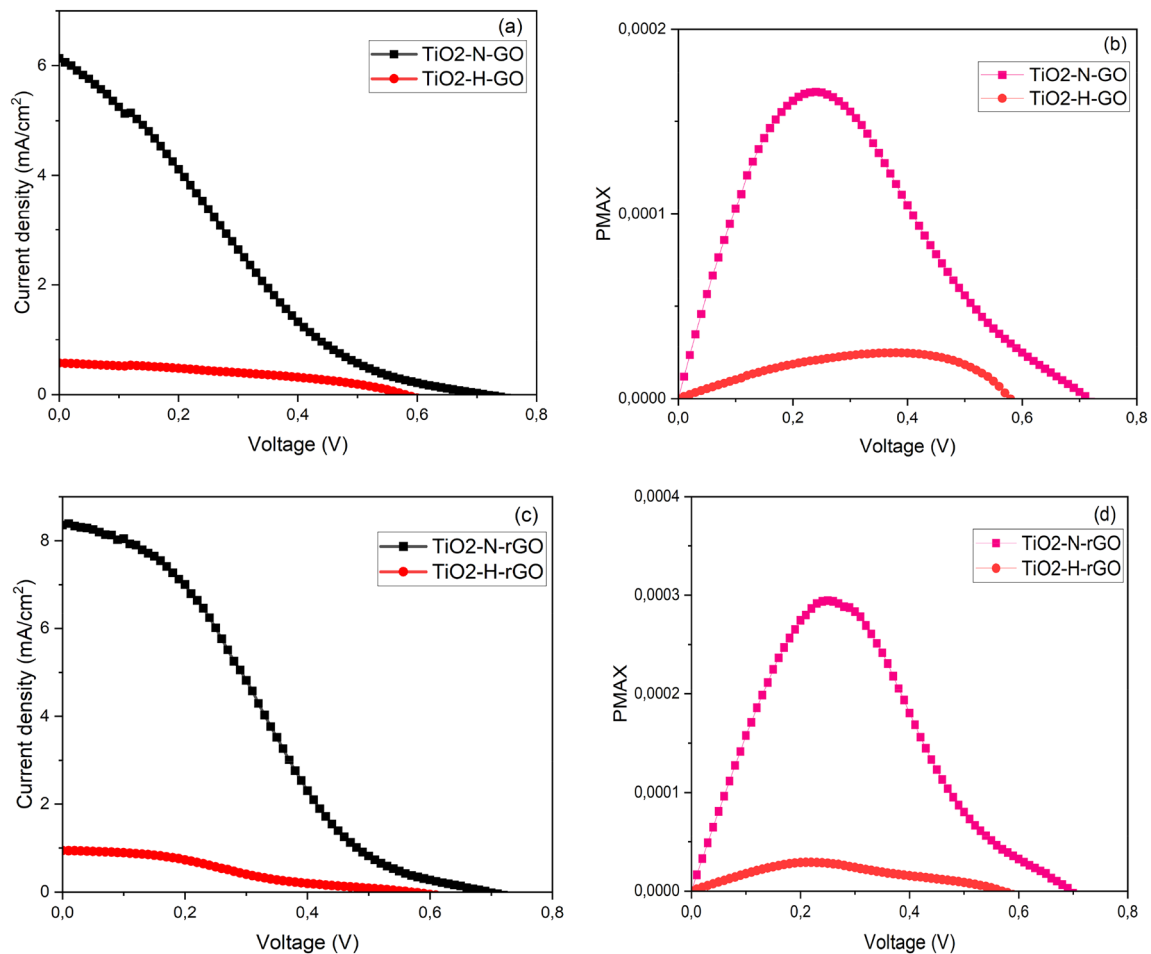


Fig. 12 J - V graph of **a** GO at the cathode, **c** rGO at the cathode DSSCs, and **b** GO at the cathode and **d** rGO DSSCs P_{MAX} - V graph

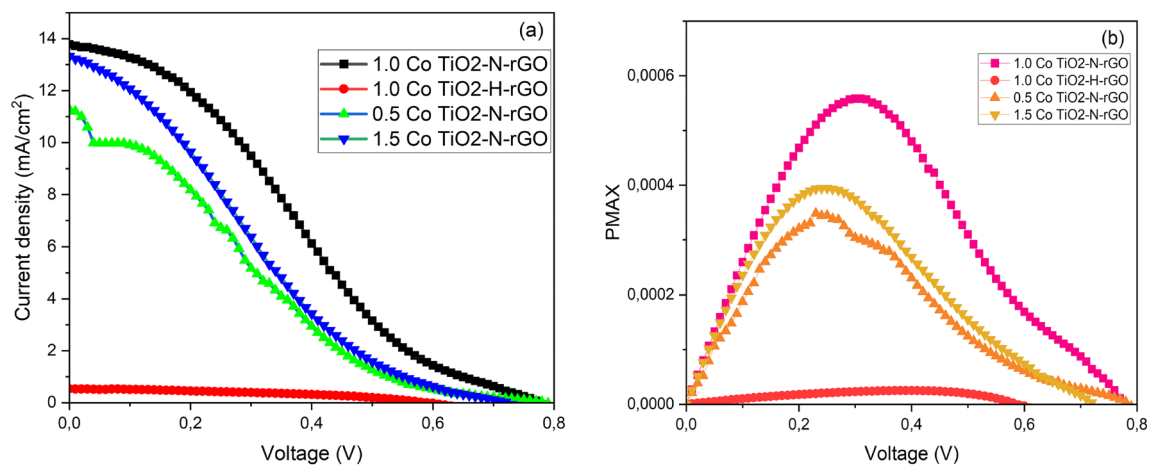


Fig. 13 **a** J - V and **b** P_{MAX} - V graphs of DSSCs of TiO_2 thin films doped with 0.5, 1.0, and 1.5% M Co^{2+}

Figure 20 shows that the DSSC encoded with 1.0 Co-N-rGO exhibits absorption in the range of 300–400 nm, with its highest efficiency reaching

16.0% at 340 nm. In contrast, the 1.0 Co-H-rGO cell demonstrates an efficiency of 4.23% at 332 nm. The DSSC encoded with 0.5 Co-N-rGO also absorbs light

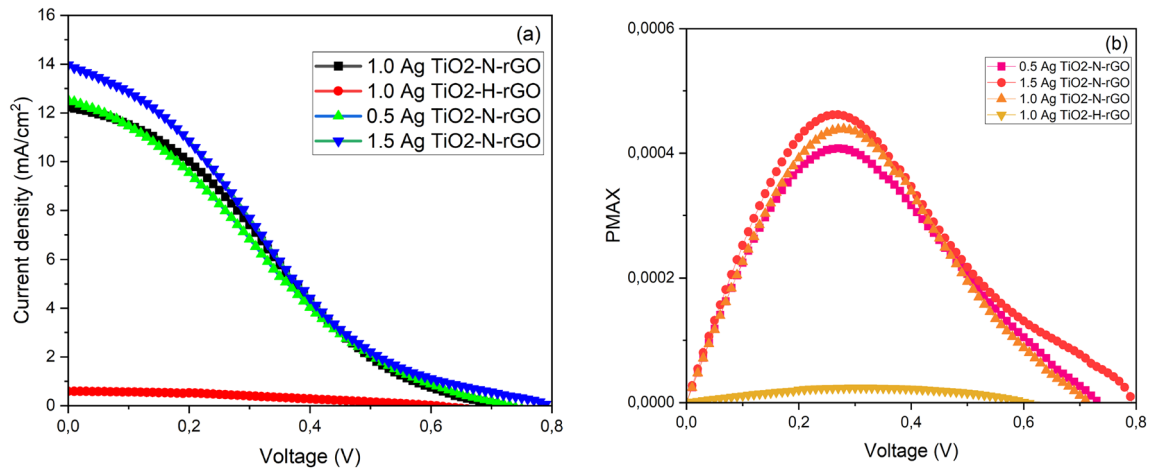


Fig. 14 $P_{\text{MAX}}-V$ graphs of **a** DSSCs and **b** TiO₂ thin films doped with 0.5, 1.0, and 1.5% M Ag¹⁺

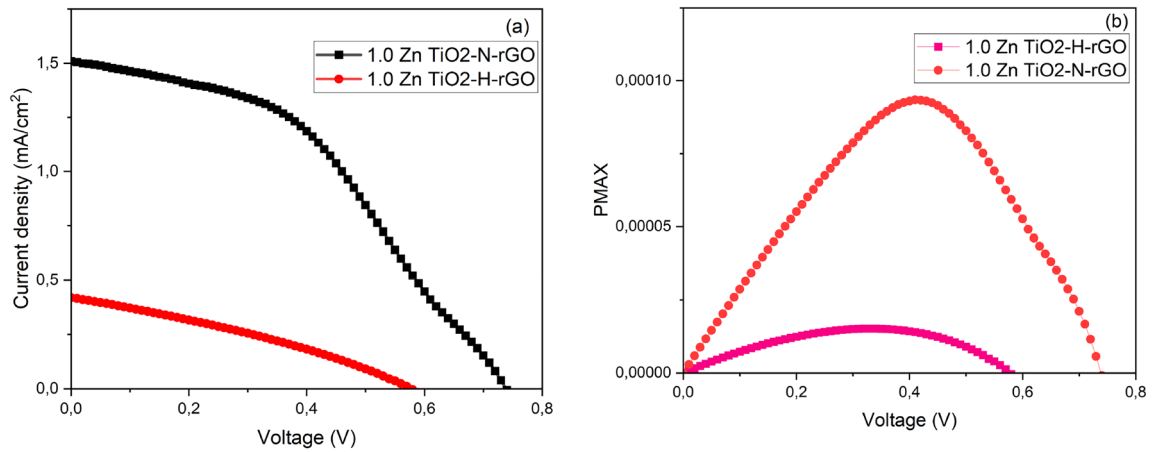


Fig. 15 **a** $J-V$ and **b** $P_{\text{MAX}}-V$ graph of DSSCs of 1.0% Zn²⁺-doped TiO₂ thin films

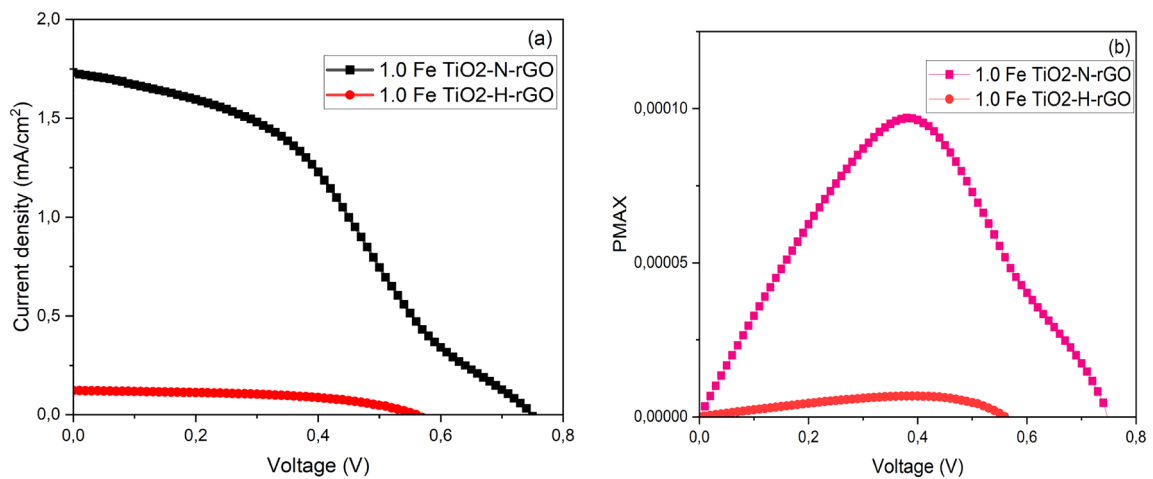


Fig. 16 **a** $J-V$ and **b** $P_{\text{MAX}}-V$ graph of DSSCs of 1.0% Fe³⁺-doped TiO₂ thin films

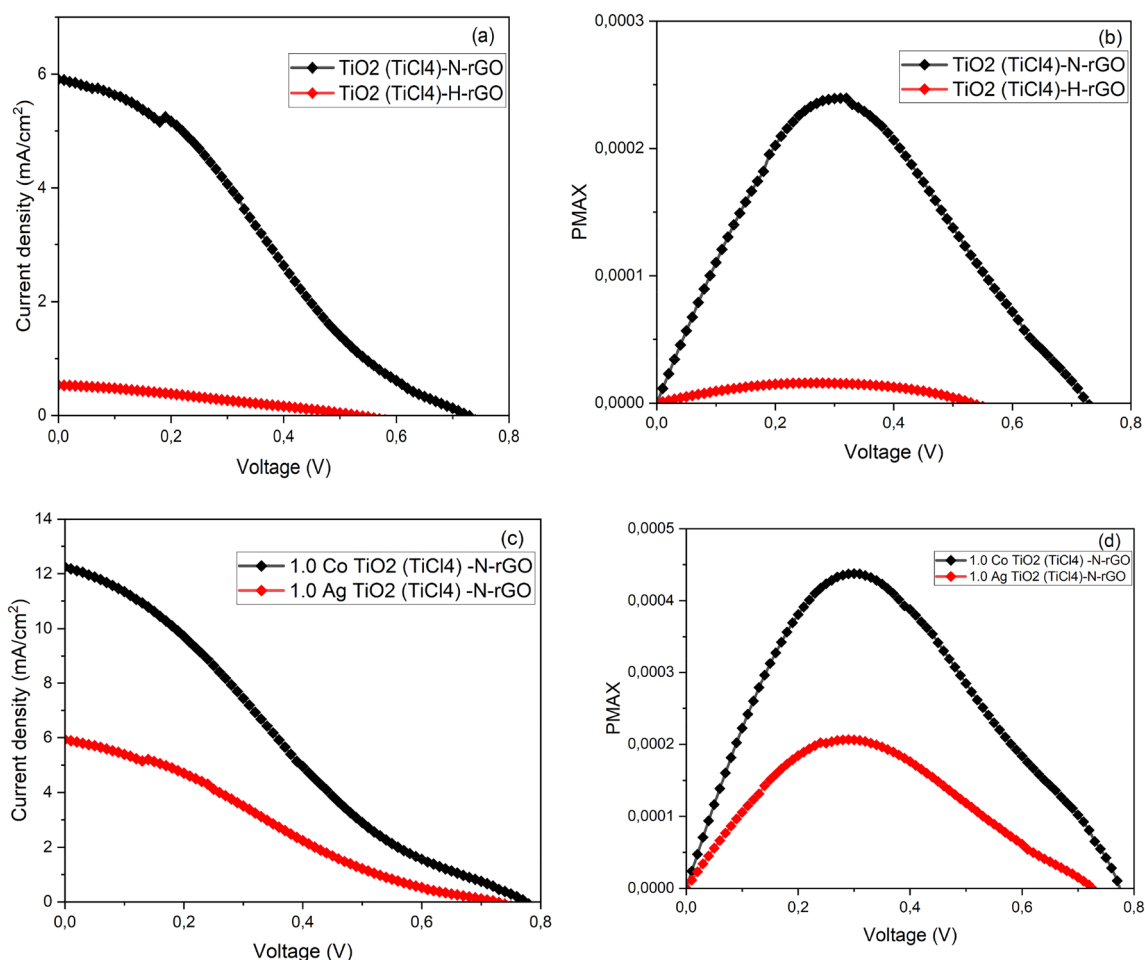


Fig. 17 (a, c) J - V and (b, d) graphs of DSSC treated with TiCl_4

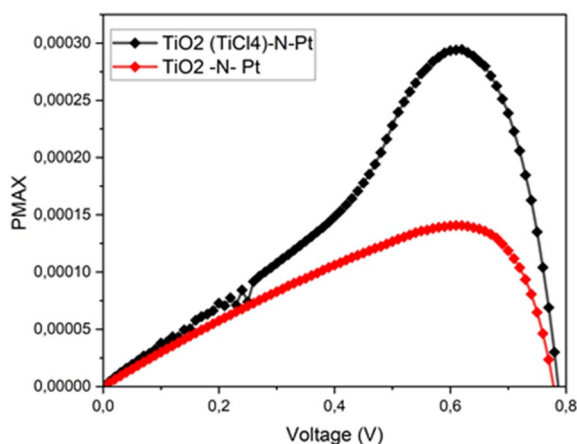


Fig. 18 P_{max} - V graph of DSSCs using Pt in the photocathode

between 300 and 400 nm, with its peak efficiency at 6.18% at 329 nm, while the 1.5 Co-N-rGO cell achieves an efficiency of 6.67% at the same wavelength.

Figure 21 demonstrates that the 1.0 Zn-N-rGO cell exhibits absorption in the range of 300–400 nm, with its peak efficiency reaching 3.39% at 337 nm. In comparison, the 1.0 Zn-H-rGO cell shows a lower absorption efficiency of 1.11% at 329 nm. Similarly, the 1.0 Fe-N-rGO cell absorbs light within the 300–400 nm range, achieving a maximum efficiency of 4.1% at 340 nm, whereas the 1.0 Fe-H-rGO cell shows an absorption efficiency of 1.15% at 340 nm.

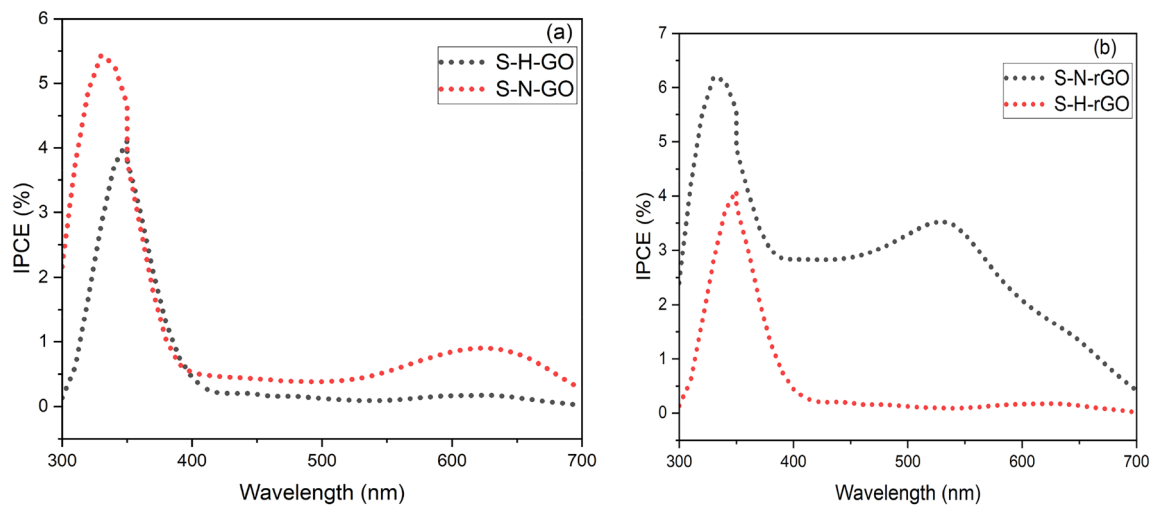
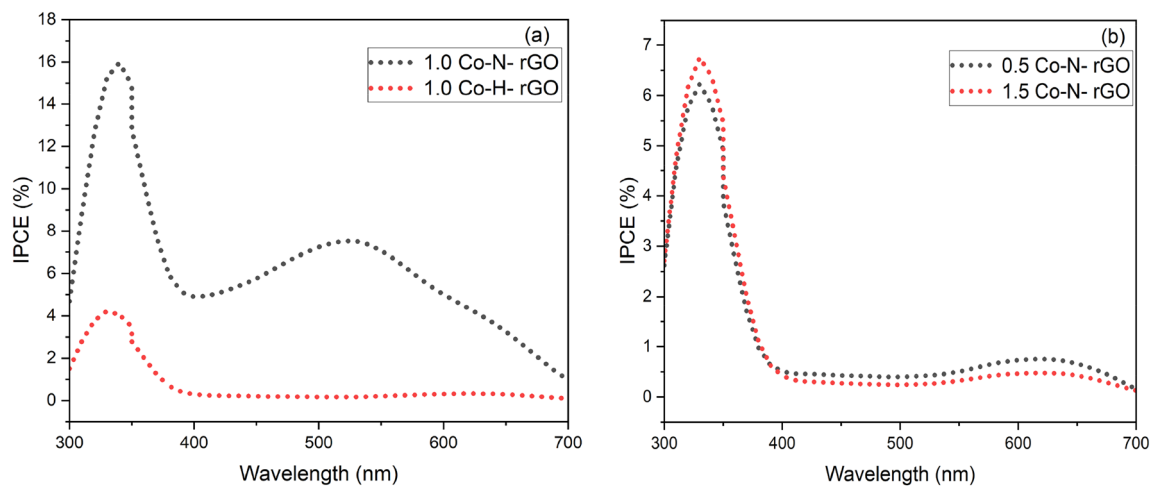
Figure 22 shows that the DSSC encoded with the Ag-N-rGO cell absorbs light in the range of 300–400 nm, achieving its highest efficiency of 17.86% at 328 nm, while the 1.0 Ag-H-rGO cell exhibits a peak efficiency of 3.97% at 347 nm. The DSSC encoded with the 0.5 Ag-N-rGO cell also absorbs light between 300 and 400 nm, with a maximum efficiency of 15.0% at 341 nm, whereas the 1.5 Ag-N-rGO cell reaches an efficiency of 12.0% at 332 nm.

Table 5 Performance results of TiCl₄-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	0.00024	0.56	1.22
TiO ₂ (TiCl ₄)-H-rGO	0.53	0.53	1.58×10^{-5}	0.56	0.25
1.0 Co TiO ₂ (TiCl ₄) -N-rGO	0.77	12.24	0.00044	0.46	2.23
1.0 Ag TiO ₂ (TiCl ₄)-N-rGO	0.72	5.93	0.00021	0.48	1.05

Table 6 Performance results of DSSCs using Pt in photocathode

Cell code	V_{OC} (V)	J_{SC} (mA/cm ²)	P_{MAX}	FF	PCE (η) (%)
TiO ₂ (TiCl ₄)-N-Pt	0.78	1.61	1.41×10^{-4}	0.99	0.72
TiO ₂ -N-Pt	0.74	2.13	2.95×10^{-4}	0.99	1.5

**Fig. 19** Photon-current conversion efficiency of S-N-GO, S-H-GO, S-N-rGO, and S-H-rGO DSSCs**Fig. 20** Photon-current conversion efficiency of 1.0 Co-N-rGO, 1.0 Co-H-rGO, 0.5 Co-N-rGO, and 1.5 Co-N-rGO DSSCs

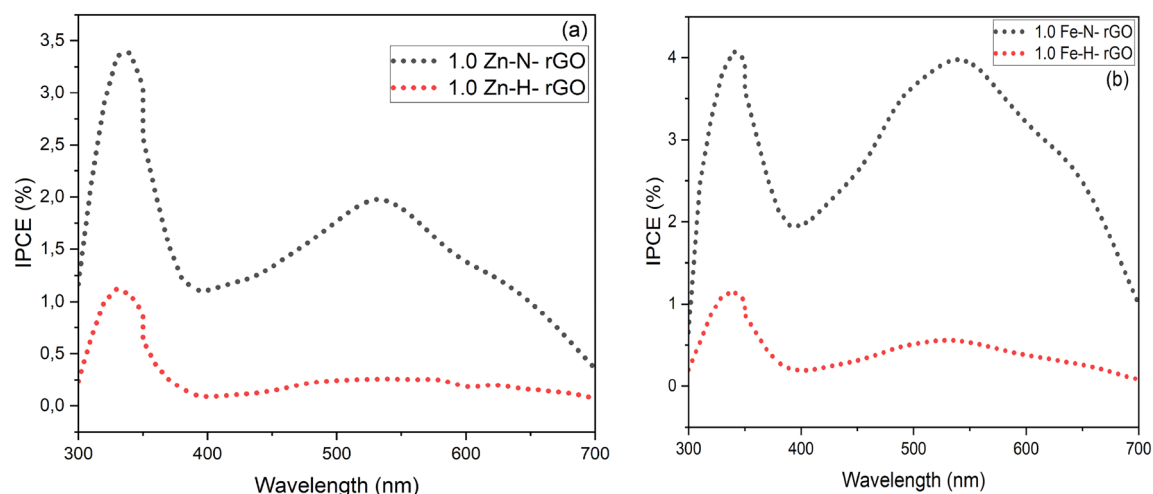


Fig. 21 Photon-current conversion efficiency of 1.0 Zn-N-rGO, 1.0 Zn-H-rGO, 1.0 Fe-N-rGO, and 1.0 Fe-H-rGO DSSCs

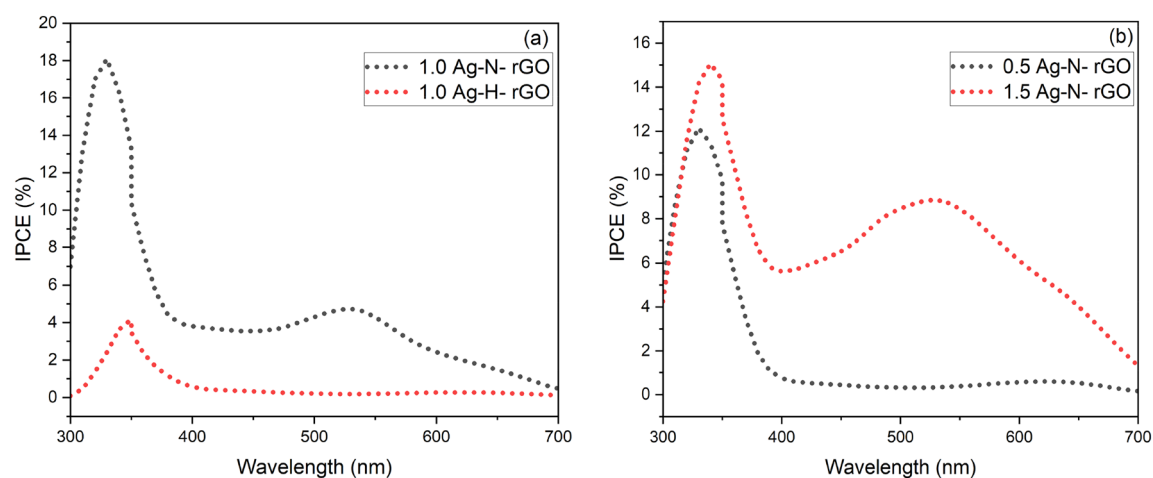


Fig. 22 Photon-current conversion efficiency of 1.0 Ag-N-rGO, 1.0 Ag-H-rGO, 0.5 Ag-N-rGO, and 1.5 Ag-N-rGO DSSCs

The incident photon number/current conversion efficiency (IPCE) results of DSSCs produced using pure and metal-doped TiO_2 thin films synthesized by the sol-gel method are given in Table 7. This table presents the IPCE values for various DSSCs with different combinations of TiO_2 films (e.g., TiO_2 -N719, TiO_2 -hibiscus) and the doping materials (GO, rGO, Co, Zn, Fe, Ag) in varying concentrations. The IPCE measurements were conducted across a range of wavelengths from 300 to 700 nm. The IPCE is a key indicator of the light-to-current conversion efficiency of the solar cell at specific wavelengths, and it provides information about how effectively the photoanode material captures and converts light into electrical energy.

The IPCE results for pure TiO_2 and metal-doped TiO_2 (Ag^{1+} , Zn^{2+} , Fe^{3+} , Co^{2+}) photoanodes showed

that doping significantly impacted the photon absorption and charge collection efficiency. The maximum IPCE value for the pure TiO_2 photoanode was observed in the UV region, as expected due to the wide bandgap of TiO_2 , which favors UV absorption. Doping with metal ions, particularly Ag^{1+} and Co^{2+} , resulted in a noticeable enhancement in the IPCE, especially in the visible light region. This suggests that doping improved the ability of TiO_2 to absorb photons in the visible spectrum, thereby extending its light absorption range. The IPCE of Ag-doped TiO_2 photoanodes was strongly influenced by the sensitizer dye. The 1.0% Ag- TiO_2 -N719-rGO cell exhibited significantly higher IPCE values across the visible spectrum, corresponding to a PCE of 17.86%, compared to the 1.0% Ag- TiO_2 -Hibiscus-rGO cell,

Table 7 Incident photon-to-current conversion efficiency (IPCE) of DSSCs using pure and 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 Co TiO ₂ -N719-rGO	1.0 Co-N- rGO	16.0
6	%1.0 M Co TiO ₂ -hibiscus-rGO	1.0 Co-H- rGO	4.23
7	%0.5 M Co TiO ₂ -N719-rGO	0.5 Co-N- rGO	6.18
8	%1.5 M Co TiO ₂ -N719-rGO	1.5 Co-N- rGO	6.67
9	%1.0 M Zn TiO ₂ -N719-rGO	1.0 Zn-N- rGO	3.39
10	%1.0 M Zn TiO ₂ -hibiscus-rGO	1.0 Zn-H- rGO	1.11
11	%1.0 M Fe TiO ₂ -N719-rGO	1.0 Fe-N- rGO	4.1
12	%1.0 M Fe TiO ₂ -hibiscus-rGO	1.0 Fe-H- rGO	1.15
13	%1.0 M Ag TiO ₂ -N719-rGO	1.0 Ag-N- rGO	17.86
14	%1.0 M Ag TiO ₂ -hibiscus-rGO	1.0 Ag-H- rGO	3.97
15	%0.5 M Ag TiO ₂ -N719-rGO	0.5 Ag-N- rGO	12.00
16	%1.5 M Ag TiO ₂ -N719-rGO	1.5 Ag-N- rGO	15.00

which showed lower IPCE and a PCE of 3.97%. The superior IPCE of N719-sensitized cells is attributed to the dye's broad visible light absorption and efficient electron injection into the TiO₂ conduction band. In contrast, the hibiscus dye shows lower photon absorption and weaker electronic coupling with TiO₂, resulting in reduced photocurrent generation. These results highlight that while Ag doping and rGO counter electrodes enhance charge transport and suppress recombination, the choice of sensitizer dye is the dominant factor determining the quantum efficiency of DSSCs.

The highest IPCE values were observed for the Co²⁺ and Ag¹⁺-doped TiO₂ photoanodes, with a substantial increase in the overall photocurrent generation, confirming the beneficial effect of these dopants on light absorption and charge transport. The increased IPCE

can be attributed to multiple synergistic effects: Ag⁺ acts as an electron trap at the TiO₂ interface, forming Schottky barriers that suppress charge recombination, while Co²⁺ introduces intermediate energy levels that extend light absorption into the visible range [42]. In addition, the doping reduces crystallite size and increases surface area, which facilitates more efficient dye adsorption and charge injection, while also altering the electronic structure and enhancing charge carrier mobility, collectively contributing to the observed increase in IPCE. Among the doped samples, the 1.0% Co²⁺ TiO₂ photoanode exhibited the highest IPCE in the UV–visible range, suggesting that the incorporation of Co²⁺ enhanced the photocatalytic properties of the TiO₂ films.

In contrast, doping with Zn²⁺ and Fe³⁺ had a less pronounced effect on the IPCE compared to Ag¹⁺ and Co²⁺, indicating that these dopants do not significantly alter the electronic properties of TiO₂ for improved light absorption and charge transport. This is consistent with the observed trends in power conversion efficiency where the Co²⁺- and Ag¹⁺-doped TiO₂ demonstrated better performance than the Zn²⁺- and Fe³⁺-doped variants.

Despite the band gap narrowing observed in Table 4, the IPCE response remains mainly in the 300–400 nm region. This behavior demonstrates that the IPCE spectrum is governed not only by the semiconductor's band gap but also by the sensitizing agent's light absorption properties and electron injection efficiency. In DSSC systems, mismatches between dye absorption spectra and electron injection efficiency can limit the IPCE response to specific wavelength regions. As can be understood from the results, photons coming onto the DSSC were converted into current more effectively with doping. In addition, more effective IPCE values were obtained in cells where N719 dye was used compared to the dye obtained from the hibiscus plant.

Overall, the IPCE measurements reinforced the findings that doping TiO₂ with specific metal ions enhances its photocatalytic activity and photon absorption capacity, thereby increasing the performance of DSSCs in terms of power conversion efficiency. These results highlight the importance of selecting appropriate dopants to enhance the light-harvesting and electron transport properties of the TiO₂ photoanodes in DSSCs.

3.11 Electrochemical impedance spectroscopy (EIS) analysis of DSSCs

The EIS analysis of DSSCs was performed at room temperature, under dark conditions, within the range

of 10^{-2} to 10^5 Hz with a potentiostat/galvanostat. The applied bias voltage was adjusted to the V_{oc} of DSSCs with an alternating current (AC) amplitude of 10 mV. The EIS spectra presented in Fig. 23 were simulated using the instrument's software and fitted

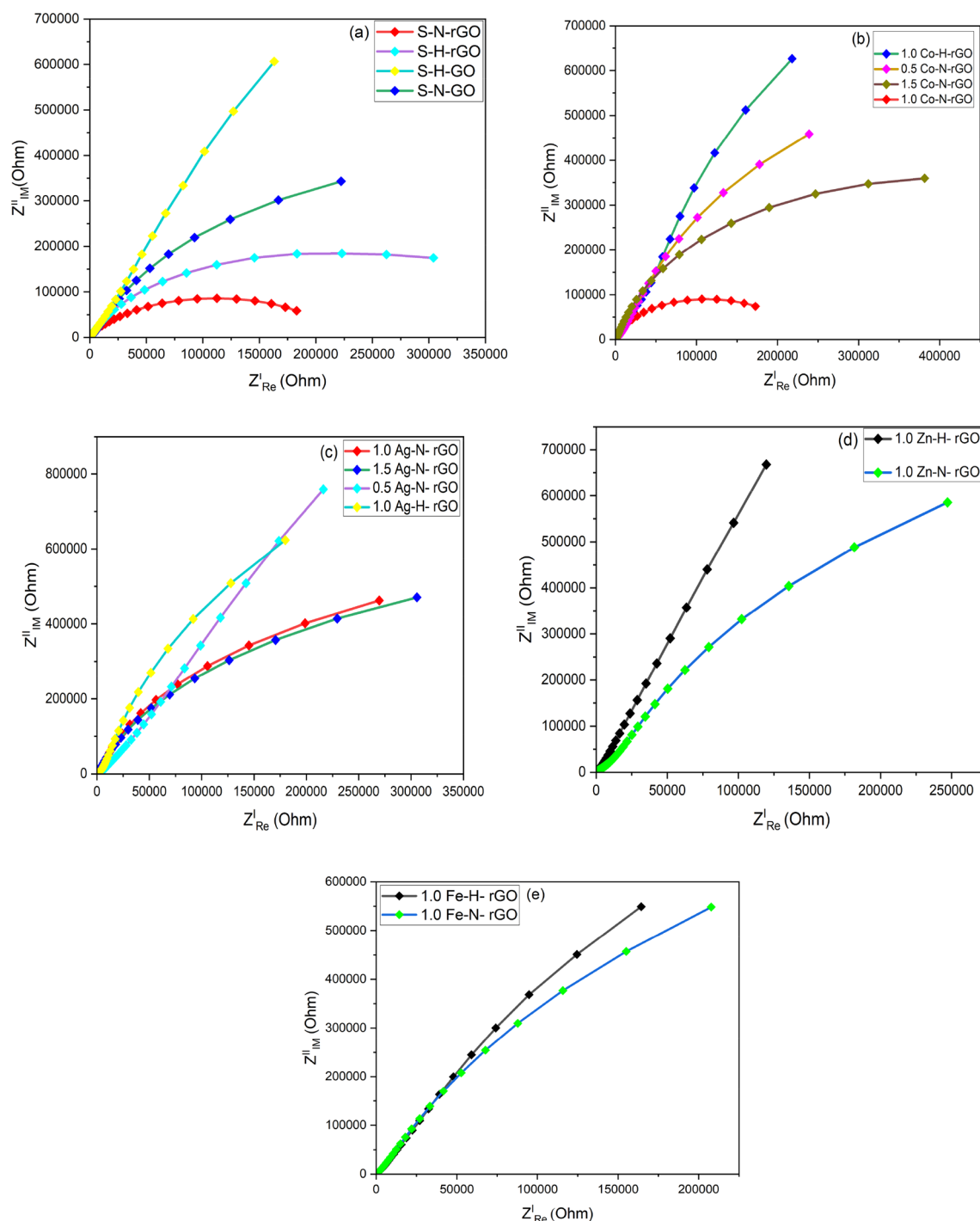


Fig. 23 Nyquist diagrams of DSSCs

to an appropriate equivalent circuit that provides the best fit to the Nyquist diagrams. The resistance values in the equivalent circuit model for each element were determined using EC-Lab software program and are summarized in Table 8.

In the circuit model shown in Fig. 24, the series resistance R_s represents the overall resistance including the sheet resistance of the TCO glass and the contact resistance of the electrolyte in the cell. The $C1/R1$ network represents the resistance of FTO/ TiO_2 /Electrolyte, $Q/R2$ represents the resistance of Electrolyte and $C2/R3$ represents the resistance of FTO/rGO/Electrolyte. The C and Q elements represent the constant phase elements (CPE) elements at the interfaces.

EIS analysis is employed to comprehensively study the kinetics of photoelectrochemical processes, including ionic and electronic activities occurring in the DSSCs of photoelectrochemical solar cells. The equivalent circuit model that fits the DSSCs is in agreement with the study by Lohar et al. (2020) [43]. Lohar et al. (2020) conducted EIS measurements both under light and dark conditions, finding that charge transfer resistance decreased under illumination. This decrease was attributed to the generation of charge carriers at the interface upon exposure to light. The solution resistance was observed to decrease after photon illumination, which was interpreted as being caused by the formation of charge carriers following the illumination. In a DSSC, three

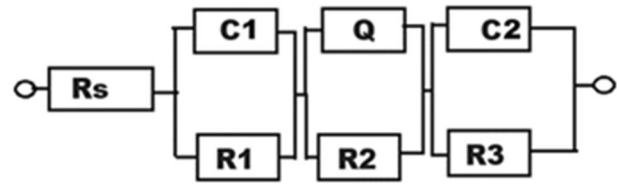


Fig. 24 Circuit model of DSSCs

main interfaces exist: FTO/ TiO_2 /dye/electrolyte, TiO_2 /dye/electrolyte, and electrolyte/rGO/FTO. These interfaces are represented by $R1$, $R2$, and $R3$, respectively. Finally, the series resistance of the cell, denoted as R_s , is the parameter that shifts the starting point of the semicircles [44]. The series resistances of the cells changed with doping; however, this change was not significant. It is considered that the resistance values are higher in the dark environment for EIS analysis because the charge carriers are not reduced in the absence of light.

EIS measurements were performed in the dark and this analysis was used to evaluate the charge transfer mechanisms and interfacial resistance in DSSCs. The decrease in charge transfer resistance and solution resistance under illumination suggests that the DSSC's performance improves with light exposure due to the generation of charge carriers. The observed higher resistance in the dark highlights the dependence of DSSC efficiency on light and the importance of optimizing the interfaces (FTO/ TiO_2 /dye/electrolyte, TiO_2 /

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 Co-N-rGO	11.64	31.54	0.017	24.28	30.8	56.86	0.167
1.0 Co-N-rGO	9.323	46.39	0.0535	39.05	50.9	29.88	0.170
1.0 Co-H-rGO	21.45	45.31	0.037	15.75	19.5	30.73	0.051
1.5 Co-N-rGO	10.94	38.69	0.105	38.54	12.6	46.54	0.123
0.5 Ag-N-rGO	19.32	22.79	1.082	35.47	9.3	10.21	0.012
1.0 Ag-N-rGO	17.02	20.85	0.616	18.22	8.3	7.386	0.0007
1.0 Ag-H-rGO	23.91	18.12	0.607	12.9	6.9	18.96	0.03713
1.5 Ag-N-rGO	11.81	13.62	4.094	28.15	10.0	24.31	1.013
1.0 Zn-N-rGO	12.2	47.67	0.310	17.19	1.5	35.58	0.0118
1.0 Zn-H-rGO	11.91	22.93	2.122	33.74	92.8	27.52	0.016
1.0 Fe-N-rGO	11.02	57.43	0.237	27.73	20.1	25.83	1.625
1.0 Fe-H-rGO	18.57	41.68	0.362	22.29	12.7	22.56	1.799

dye/electrolyte, and electrolyte/rGO/FTO) for better charge transport and overall performance. The series resistance, although slightly affected by doping, is less critical compared to other resistances in determining the efficiency of DSSCs. Therefore, enhancing charge transfer through interface engineering and improving light absorption remain key strategies for optimizing DSSC performance.

4 Conclusion

This study investigates the synthesis and characterization of TiO_2 thin films doped with various metal ions (Ag^+ , Zn^{2+} , Fe^{3+} , Co^{2+}) and their application in dye-sensitized solar cells (DSSCs). The results reveal the following key findings:

- Metal doping modified the morphology and crystal structure of TiO_2 films. SEM, XRD, and XPS analyses confirmed that the anatase phase was preserved, while slight peak shifts and crystallite size reduction indicated lattice distortion caused by dopant incorporation.
- BET and UV–visible analyses showed improved surface properties and enhanced light absorption in the visible region, promoting better dye adsorption and photon harvesting.
- Photovoltaic results revealed that metal doping significantly influenced DSSC performance. The 1.0% Co^{2+} -doped TiO_2 photoanode combined with the rGO counter electrode exhibited the highest efficiency of 2.85%, attributed to improved charge transport and reduced recombination.
- rGO counter electrodes demonstrated high electrical conductivity and effective electrocatalytic activity, indicating their potential as a low-cost alternative to Pt-based counter electrodes.
- TiCl_4 surface treatment produced mixed effects, suggesting that optimization of treatment conditions is necessary for further performance improvement.

In conclusion, metal-doped TiO_2 films, especially with Co^{2+} and Ag^+ doping, alongside the use of rGO as a CE, show promising potential for enhancing the efficiency and performance of DSSCs. The findings of this study provide valuable insights for developing low-cost, high-performance DSSCs for future solar energy applications.

Author contributions

Berrak Caliskan contributed to conceptualization, investigation, methodology, supervision, project administration, writing—original draft, and writing—review and editing. Enes Sayan contributed to conceptualization, supervision, project administration, and writing—review and editing. Erdal Igman contributed to supervision and writing—review and editing.

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Data availability

Data will be made available on request.

Declarations

Conflict of interest The authors declare no competing interests.

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