

Effect of photoanode structure and sensitization conditions on the photovoltaic response of dye-sensitized solar cells

Paweł Gnida^a, Aneta Slodek^b, Ewa Schab-Balcerzak^{a,b*}

^a Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowska St., 41-819 Zabrze, Poland

^b Institute of Chemistry, University of Silesia, 9 Szkolna St., 40-006 Katowice, Poland

Article info

Article history:

Received 7 Oct. 2021

Received in revised form 21 Jan. 2022

Accepted 21 Jan. 2022

Available on-line 10 Mar. 2022

Keywords:

Dye-sensitized solar cells; N719; phenothiazine derivatives; TiO₂ nanostructures; co-sensitization; co-adsorbents.

Abstract

This work summarises investigations focused on the photoanode impact on the photovoltaic response of dye-sensitized solar cells. This is a comparison of the results obtained by the authors' research team with literature data. The studies concern the effect of the chemical structure of the applied dye, TiO₂ nanostructure, co-adsorbents addition, and experimental conditions of the anode preparation. The oxide substrates were examined using a scanning electron microscope to determine the thickness and structure of the material. The TiO₂ substrates with anchored dye molecules were also tested for absorption properties in the UV-Vis light range, largely translating into current density values. Photovoltaic parameters of the fabricated devices with sandwich structure were obtained from current-voltage measurements. During tests conducted with the N719 dye, it was found that devices containing an 8.4 μm thick oxide semiconductor layer had the highest efficiency (5.99%). At the same time, studies were carried out to determine the effect of the solvent and it was found that the best results were obtained using an ACN:tert-butanol mixture (5.46%). Next, phenothiazine derivatives (PTZ-1–PTZ-6) were used to prepare the devices; among the prepared solar cells, the devices containing PTZ-2 and PTZ-3 had the highest performance (6.21 and 6.22%, respectively). Two compounds designated as Th-1 and M-1 were used to prepare devices containing a dye mixture with N719.

1. Introduction

Solar energy is considered to be the most promising of all renewable energy sources. The use of solar radiation to produce electricity, i.e., the photovoltaic effect, is already playing an important role today. Currently, photovoltaic (PV) technologies can be divided into three groups among which the third-generation solar cells based on organic materials are beginning to play an increasingly important role. [1] Dye-sensitized solar cells (DSSCs) are of particular interest for their wide practical applications. The first experiments with dye-sensitized solar cells were carried on in the 1960s and 1970s [2, 3]. However, the first efficient DSSC was presented by Graetzel and O'Regan in 1991 [4]. The unquestionable advantages of this device are its ability to operate at wide angles of incidence, good efficiency at low irradiance, ability to colour and transparency change,

and low-complexity manufacturing methods, which translates into relatively low production costs. Currently, the maximum efficiency of DSSCs is 14.2% [5].

The performance of DSSCs depends in a complex way on both the type of materials used and the preparation of individual solar cell components. The aim of the study was to determine the influence of photoanode preparation and construction conditions on the photovoltaic response of devices. Experimental aspects of the photoanode preparation included the determination of correlation between the applied conditions for the anode dye sensitization and the thickness of the mesoporous TiO₂ layer [6–9]. The photoanode structure was modified by using various TiO₂ nanostructures [10–12] and dyes, as well as by the addition of co-adsorbents [6, 12–15]. The oxide nanostructures are added mainly to develop a surface to which dye molecules can anchor and improve electronic conductivity. [10, 12] It is also worth noting a very important publication that very clearly shows how important the development of the photoanode oxide surface

*Corresponding author at: ewa.schab-balcerzak@us.edu.pl or eschab-balcerzak@cmpw-pan.edu.pl

<https://doi.org/10.24425/opelre.2022.140739>

1896-3757/ Association of Polish Electrical Engineers (SEP) and Polish Academic of Sciences (PAS). Published by PAS

© 2022 The Author(s). This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

is in correlation to the photovoltaic parameters of the solar cell. [16] The addition of co-adsorbents to the dye solution prevents the formation of aggregates on the semiconductor surface, increasing the current density and decreasing the resistance [15, 17, 18]. Moreover, dye mixtures were used for the anode sensitization [19–21]. Similar studies with the N719 dye have been extensively carried out in the literature, among others, Refs. 18, 22–24 can be cited. In addition, much attention is now being paid to the process of co-sensitization of metal-free dyes [25, 26]. The influence of the above-mentioned factors on the absorption properties in the UV-Vis light range of the photoanode, its surface morphology, and the PV parameters determined from the current-voltage characteristics (open-circuit voltage, V_{oc} , short-circuit current density, J_{sc} , fill factor, FF , and power conversion efficiency, PCE) of solar cells with the FTO/TiO₂+dye/EL-HSE/Pt/FTO structure was analysed. Additionally, the electron generation efficiency as a function of the wavelength of the incident photon to the current efficiency (IPCE) was determined for selected DSSCs.

2. Effect of experimental conditions on the photoanode preparation

The effects of TiO₂ thickness (4.5, 7.3, 8.4, and 15.0 μm), type of solvent (MeOH, DMF, and ACN:*t*-BuOH), time of immersion of the electrode in the dye solution (24, 48, and 72 h), and addition of co-adsorbents (chloric acid, CA, deoxycholic acid, DCA, and chenodeoxycholic acid, CDCA) were taken into account in the present study [6]. A commercial dye di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719) was used to prepare the tested solar cells.

The thickness of TiO₂ layers was determined by SEM measurements (Fig. 1).

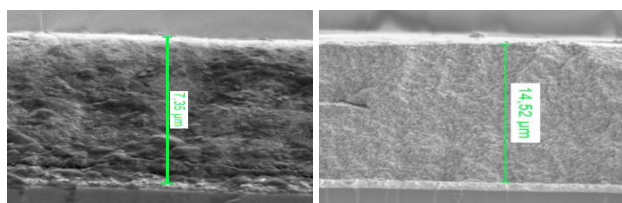


Fig. 1. The SEM cross-sectional images of the tested photoanodes [6].

The effect of the TiO₂ layer thickness on the roughness factor (root mean square – RMS) determined from AFM measurements was observed, the value of which increased (from 36 to 86 nm) with the layer thickness. The photoanodes with TiO₂ thicknesses of 7.3 and 8.4 μm showed the most favourable UV-Vis properties which translated into IPCE values. Good absorption properties, including a wide range of sunlight absorption, have a decisive influence on the current density generated during the process, translating into the efficiency of the entire solar cell. However, the current densities in DSSCs are also influenced by the interfaces energy losses which are associated with the shunt (R_{SH}) and series (R_S) resistances of the devices [27]. It was found that the resistances for authors' devices reported in Ref. 6 depended on the thickness of the metal oxide (TiO₂ = 4.5 nm: $R_{SH} = 2071 \Omega \cdot \text{cm}^2$, $R_S = \Omega \cdot \text{cm}^2$; TiO₂ = 7.3 nm: $R_{SH} = 2653 \Omega \cdot \text{cm}^2$, $R_S = 82 \Omega \cdot \text{cm}^2$; TiO₂ = 8.4 nm:

$R_{SH} = 3182 \Omega \cdot \text{cm}^2$, $R_S = 67 \Omega \cdot \text{cm}^2$; TiO₂ = 15 nm: $R_{SH} = 2222 \Omega \cdot \text{cm}^2$, $R_S = 61 \Omega \cdot \text{cm}^2$). The application of TiO₂ thicknesses of 7.3 and 8.4 μm increased the shunt resistance and decreased the series resistance compared to a TiO₂ thickness of 4.5 μm . Device with a TiO₂ thickness of 8.4 μm showed R_{SH} increased by 53% and lowered R_S by 37% over to cell with a thickness of 4.5 μm . The decrease of R_S suggests a better electrical contact between the TiO₂ and FTO surface, whereas the increase of R_{SH} confirms a better resistance to the electron loss to parasitic processes. Together with an increase of R_{SH} and a drop of R_S , an increase of PCE was seen. Registered PV parameters of the fabricated devices consisting of the reference dye (N719) are shown in Table 1.

Table 1.
Photovoltaic parameters of fabricated solar cells.

Parameter	V_{oc} [mV]	J_{sc} [mA·cm ⁻²]	FF [-]	PCE [%]	Ref.
TiO ₂ thickness [μm]	4.5	689	13.66	0.44	4.20 [6]
	7.3	720	17.42	0.44	5.75
	8.4	762	14.34	0.54	5.99
	15.0	733	13.60	0.57	5.80
	3.5	733	7.36	0.47	2.51 [7]
	6.0	756	11.14	0.54	4.49
	8.0	746	12.42	0.56	5.02
	10.0	793	12.75	0.59	5.93
	12.0	763	11.81	0.59	5.15
	14.0	742	8.28	0.57	3.24
	6.0	680	3.60	0.50	1.20 [8]
	10.0	690	4.30	0.50	1.44
	14.0	710	3.30	0.42	1.00
	8.7	628	9.40	0.64	3.89 [9]
	10.2	652	10.10	0.63	3.99
	11.6	669	12.50	0.66	5.52
	13.1	661	8.80	0.64	3.74
	14.5	619	2.90	0.69	2.20
	MeOH (24 h)	562	14.73	0.36	3.20 [6]
	DMF (24 h)	664	12.22	0.55	4.45
ACN: <i>t</i> -BuOH (24 h)	730	13.19	0.56	5.46	
ACN: <i>t</i> -BuOH (72 h)	698	21.34	0.41	6.30	

The TiO₂ with a thickness of 8.4 μm was used to prepare the anode for further studies due to the highest solar cell performance. It is worth comparing the obtained results showing the influence of the oxide semiconductor layer thickness on the PV performance. In the cited works [7–9], the studies were also based on commercially available Ru-dyes (N719 [7, 9] or N3 [8]). In Refs. 7–9, the TiO₂ thickness was in the range of 3.5 to 14.5 μm . As shown in Table 1, the best photovoltaic performance was obtained for TiO₂ layers with thicknesses in the range of 8.5 to 10 μm . Each time, a decrease in the current density can be observed for the thickest TiO₂ layers. In Ref. 6, however, it was found that the amount of adsorbed dye molecules was

the highest for a substrate with a thickness of 15 μm . This may be caused by the TiO_2 layer being too thick which hinders the absorption of photons by the dye and can cause reflection and scattering. Considering the effect of the type of solvent used to prepare the dye solution, it was found that the use of the ACN:*t*-BuOH solvent mixture provided the solar cell with the highest number of anchored dye molecules ($2.95 \cdot 10^{-7} \text{ mol} \cdot \text{cm}^{-2}$) to be obtained with the highest IPCE and PCE values. As the anode immersion time in the solution was increased from 24 to 72 h, the PCE value increased by 66, 40 and 15% in MeOH, DMF, and ACN:*t*-BuOH, respectively. The differences in efficiencies of cells prepared with different solvents and the amount of anchored dye molecules can be explained by considering the donor-acceptor reaction between solvents and hydroxyl surface groups of TiO_2 [28]. The so-called donor number (DN) of the solvent was found to be particularly important for the interactions between the solvent and the hydroxyl surface groups of TiO_2 . The donor number of MeOH, DMF, ACN, and *tert*-butanol is 19, 26.6, 14.1, and 38 $\text{kcal} \cdot \text{mol}^{-1}$, respectively [28]. It can be concluded that solvents with a higher DN value will cause more dye molecules to anchor to the TiO_2 surface [28].

Studies on the effect of the co-adsorbent addition showed an improvement in PV performance when CDCA was used, and the PCE conversion efficiency increased from 5.96 to 6.22%.

3. Effect of dyes chemical structure

Synthesized phenothiazine derivatives of the chemical structure shown in Fig. 2 [21, 30, 31] were used to prepare the DSSC devices. The results obtained on the construction of the photoanode prepared by using the reference dye (N719) were taken into account in the preparation of the solar cells.

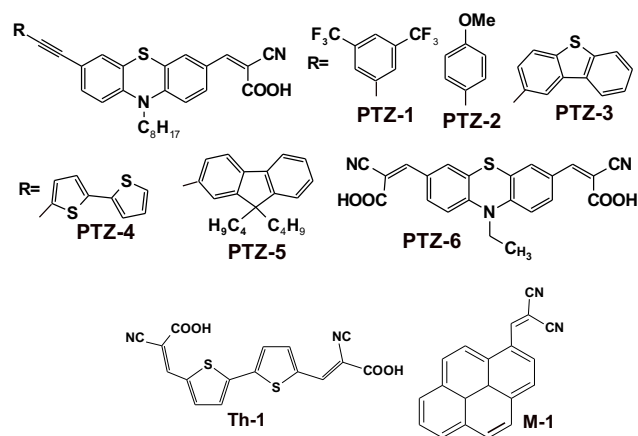


Fig. 2. Chemical structure of compounds tested in DSSCs [19–21, 30, 31].

Taking into account the current research trends, it is worth noting that phenothiazine derivatives are increasingly investigated in photovoltaic devices [32–35]. The great advantage of this group of compounds is the high electron-donating capacity and the non-planar butterfly conformation which hinders the molecular aggregation. In addition, it is important that phenothiazine derivatives can be relatively easily obtained and modified, often at low cost

and with a low environmental impact [36]. The effect of the structure of the substituent $-\text{R}$ in the acetylene bond on the electronic absorption properties and the energies of the limiting molecular orbitals of the synthesized dyes was observed, as shown in Fig. 3.

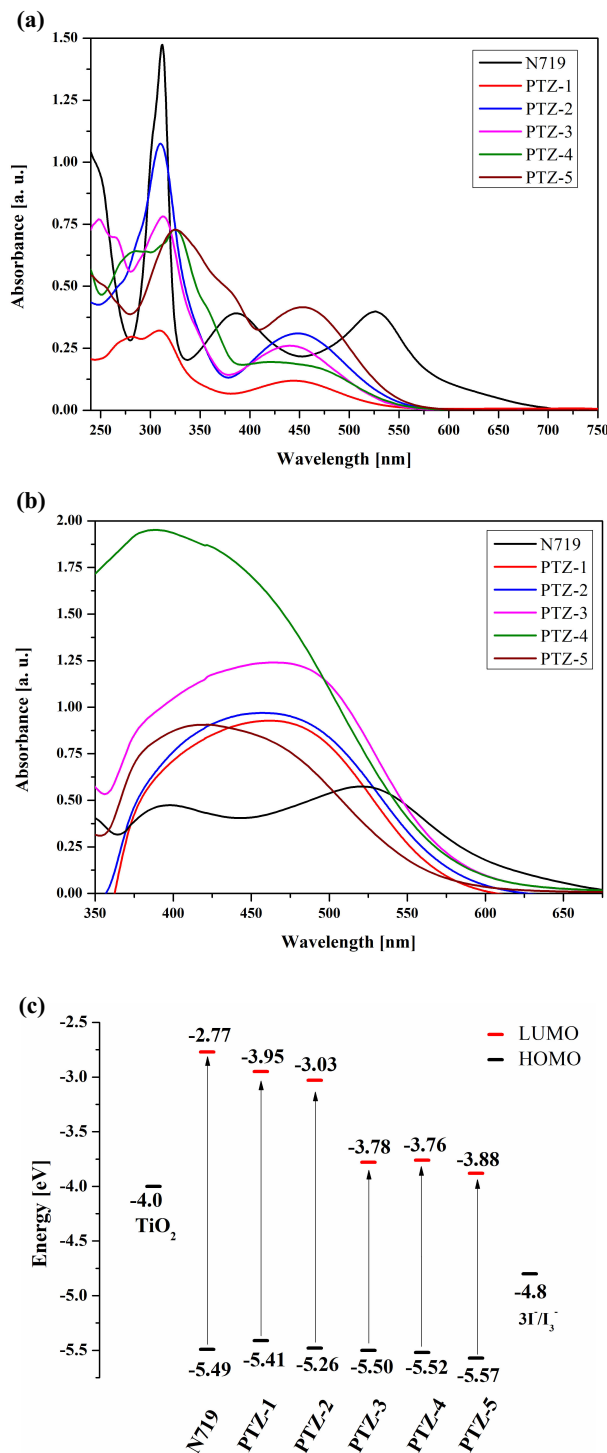


Fig. 3. UV-Vis spectra of PTZ-1–PTZ-5 in chloroform (a), TiO_2 with adsorbed dye molecules (b), and scheme of energy levels of the solar cell components (c) [30, 31].

The photoanodes containing phenothiazine derivatives (PTZ-1–PTZ-5) showed lower RMS values ($\sim 18 \text{ nm}$) and absorbed light more intensively in the range from 350 to 600 nm compared to the anode sensitized with N719 (RMS = 86 nm) [(Fig. 3(b)]. The PCE conversion efficiency of the solar cells sensitized with phenothiazine

derivatives with acetylene bonding was higher than that of the reference device containing N719 (Table 2). Only when PTZ-6 was used, the cell efficiency was marginally lower than the reference solar cell.

Table 2.
Photovoltaic parameters of DSSCs containing new phenothiazine derivatives and their mixtures with N719 with the reference device.

Dye	V_{oc} [mV]	J_{sc} [mA·cm ⁻²]	FF [-]	PCE [%]	Ref.
N719	631	12.34	0.46	3.56	[30]
PTZ-1	730	15.38	0.45	5.03	
PTZ-2	759	16.74	0.49	6.21	
PTZ-3	700	17.96	0.48	6.22	[31]
PTZ-4	631	11.87	0.54	4.22	
PTZ-5	703	12.08	0.56	4.80	
N719	664	12.22	0.55	4.45	[21]
PTZ-6	650	17.27	0.42	4.85	
N719/PTZ-6	668	19.65	0.41	5.60	
PTZ-7	710	10.80	0.69	5.35	[33]
PTZ-8	640	10.06	0.69	4.43	
W21	610	14.20	0.67	5.80	[34]
W22	640	13.50	0.66	5.70	
W23	670	13.00	0.66	5.75	
D1	780	16.66	0.68	8.80	[35]
D2	800	16.73	0.68	9.05	
D3	750	14.70	0.71	7.83	
D4	770	14.42	0.71	7.90	
N719	718	20.40	0.40	5.75	[19]
N719/Th-1	655	20.98	0.45	6.30	
N719	747	19.64	0.46	6.84	[20]
N719/M-1	726	18.18	0.50	6.78	
N719	658	18.59	0.62	7.61	[37]
N719/IS1	660	10.62	0.63	4.35	
N719/IS2	668	15.45	0.64	6.61	
N719/IS3	663	17.20	0.62	7.08	
N719/IS4	671	18.77	0.61	7.69	
N719/IS5	680	19.23	0.62	8.09	
N719	760	12.29	0.74	6.90	[24]
N719/D35 (0.4:0.1)	770	12.70	0.74	7.20	
N719/D35 (0.3:0.2)	780	13.39	0.76	8.00	
N719/D35 (0.2:0.3)	750	13.73	0.74	7.60	
N719/D35 (0.1:0.4)	760	13.76	0.71	7.40	
N719	666	16.90	0.65	7.28	[38]
N719/AZ5	698	17.90	0.63	7.91	

The use of phenothiazine derivatives in DSSCs is currently increasingly explored, although it is still often theoretical [39–41]. Both the research conducted by authors' team and most of literature reports point to phenothiazine derivatives as a good alternative to metal- dyes. In the works cited, high efficiencies of the studied cells can be observed, in most cases exceeding 5%. In Ref. 35, high

values of V_{oc} (750–800 mV) can be observed, indicating a very good match between the fermi level of the oxide semiconductor-dye system and the redox potential of the electrolyte. In many cases, DSSCs containing phenothiazine derivatives show higher efficiencies than reference solar cells prepared with the same methods.

Studies have also been carried out on mixtures of synthesized dyes with N719 to reduce the amount of commercial dye used while maintaining their performance [19–21, 24, 37, 38]. In addition, in the case of the mixture of N719 with a bithiophene derivative, the preparation of the solution was examined, taking into account the order of addition of each dye: PTZ-6, Th-1, or M-1 (Th-1 and M-1 in Fig. 2 [19–21]). The highest PCE (6.30%) was observed in the solar cell where the anode was immersed in the mixture of N719 and Th-1. Initial immersion of the anode in the N719 solution for 48 h, then in the Th-1 solution, and repeating the process on a new medium in the reverse order of dipping caused the fabricated device PCE to drop to 2.27 and 3.20%, respectively. The use of dye mixtures had a beneficial effect on the PV parameters of the solar cells, increasing or maintaining the PCE at the same level. Appearing differences in PV parameters of solar cells sensitized with N719 are due to the use of different solvents to prepare the dye solution caused by the need of the solvent selection, taking into account the solubility of the synthesized compounds (PTZ-6, Th-1, and M-1). Of course, it should be borne in mind that the use of co-sensitization does not always increase efficiency, as indicated, among others, in Refs. 20 and 37. The application of the co-sensitization process is aimed at extending the range of light absorption by the cell, which largely translates into an increase in the density of the generated current and may also cause an increase in the quasi-fermi level, thus, increasing the difference between the redox potential of the electrolyte which will translate into an increase in V_{oc} [42]. As can be seen from Ref. 24, the efficiency of the cell containing two dyes may be even more than 1% higher than for the reference dye (an increase from 6.90 to 8.00%), given the significant limitation of its use.

4. Effect of TiO₂ nanostructure

Three types of TiO₂ nanostructures were investigated: nanoparticles (NP), nanowires (NW), and nanotubes (NT). SEM studies showed that the prepared oxide layers had similar thicknesses of 10.15 (NP), 11.4 (NP/NW), and 11.15 μm (NP/NT). On the other hand, the difference was observed in the RMS values, 20, 150, and 35 nm for NP, NP/NW, and NP/NT, respectively. The surface morphology of TiO₂ from N719 was also investigated using an optical microscope (Fig. 4). Other examples can be found in the literature comparing TiO₂ nanostructures and their impact on device performance. In Ref. 10, the prepared TiO₂ nanostructures such as nanoparticles (TNP), nanoflakes (TNF), and nanotubes (TNT-1) were compared with the commercial TiO₂ nanoparticles (P25) often used in DSSC. The spherical TiO₂ nanoparticles (GSS) obtained by the research team, as well as the rod-shaped (GSR) and wire-shaped (GSW) were also investigated in Ref. 11. In all cited works on the effect of the TiO₂ nanostructure on device performance, the commercial dye N719 was used for the solar cell preparation.

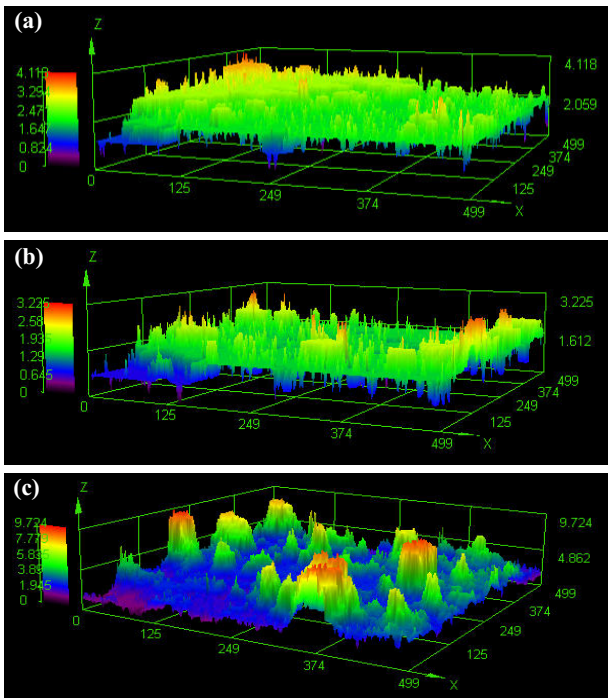


Fig. 4. The optical microscope images of different TiO₂ nanostructures with N719: NP (a), NP/NT (b), and NP/NW (c) [12].

UV-Vis investigations of TiO₂ layers with the adsorbed N719 showed similar and definitely better absorption properties of photoanodes with NP and NP/NT compared to NP/NW (Fig. 5).

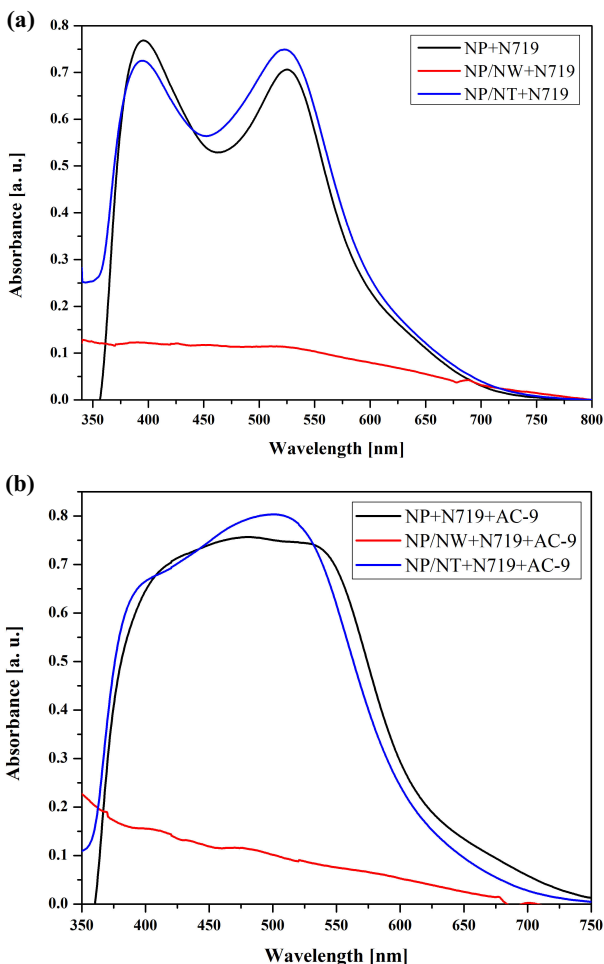


Fig. 5. UV-Vis spectra of different TiO₂ nanostructures sensitized with N719 (a) and N719+AC-9 (b) [12].

Compared to the others, the layers with NW were characterized by a lower capacity to adsorb N719, confirmed by desorption studies. Considering the photovoltaic response of cells with N719 returning different TiO₂ nanostructures, the beneficial effect of the presence of NT became apparent (Table 3), which resulted in a 36% increase in PCE.

Table 3. PV parameters of DSSCs containing different TiO₂ nanostructures.

TiO ₂ +dye	V _{oc} [mV]	J _{sc} [mA cm ⁻²]	FF [-]	PCE [%]	Ref.
NP/N719	720	15.80	0.44	5.10	[12]
NP/PTZ-6	675	10.54	0.58	4.21	
NP/N719/PTZ-6	730	15.06	0.54	6.10	
NP/N719/PTZ-6/CDCA	732	15.20	0.59	6.69	
NP/NW/N719	738	8.89	0.62	4.15	
NP/NW/PTZ-6	697	5.90	0.61	2.50	
NP/NW/N719/PTZ-6	740	11.48	0.57	4.90	
NP/NW/N719/PTZ-6/CDCA	740	11.34	0.63	5.44	
NP/NT/N719	725	16.27	0.46	5.56	
NP/NT/PTZ-6	678	10.71	0.61	4.56	
NP/NT/N719/PTZ-6	714	16.33	0.54	6.48	
NP/NT/N719/PTZ-6/CDCA	711	16.60	0.58	6.97	
P25/N719	704	10.39	0.64	4.68	[10]
TNP/N719	746	10.95	0.66	5.39	
TNF/N719	728	12.90	0.68	6.39	
TNT-1/N719	748	13.75	0.70	7.20	
P25/N719	730	7.40	0.74	4.00	[11]
GSS/N719	728	9.90	0.73	5.30	
GSR/N719	733	8.30	0.77	4.70	
GSW/N719	735	7.60	0.75	4.20	

Additionally, the effect of TiO₂ nanostructures on the photovoltaic response of DSSCs was tested in solar cells using the synthesized dye PTZ-6, its mixture with N719, and the addition of CDCA to the dye mixture. Figure 5 shows the current-voltage characteristics of devices containing TiO₂ spherical nanoparticles with the addition of nanotubes (NP/NT). The photocurrent density–voltage (*J*–*V*) curves of the prepared devices containing NP/NT nanostructures are shown in Fig. 6 [12].

The obtained results confirmed the observed regularity, i.e., the application of NPs with NT TiO₂ decreased the PCE values. It was shown that the NP/NT-modified titanium oxide was the most effective electrode, probably due to the high active surface area which can be confirmed by dye loading values being the highest and easy charge transfer. Referring to the results obtained in Ref. 12 to the cited literature [10, 11], it can be observed that the values of the generated current density increase with the development of the surface of the oxide structures. In particular, the results from Refs. 10 and 12, where the highest values of

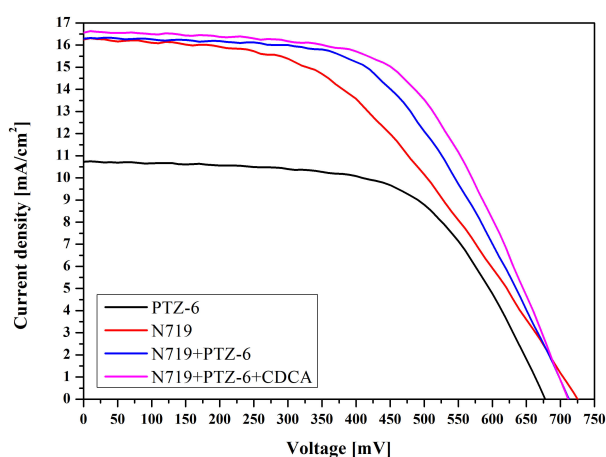


Fig. 6. Photocurrent density–voltage (J – V) curves of the prepared solar cells containing NP/NT nanostructures [12].

the generated current density are recorded for substrates containing TiO₂ nanotubes, are consistent with each other. This is most likely due to the ability to anchor dye molecules both from the outside of the nanotube and from the inside. It can be seen very well by comparing the amount of the adsorbed dye on the oxide substrate. In Ref. 12, the desorption of the dye N719 was carried out and the following values were obtained: $4.04 \cdot 10^{-8}$, $3.77 \cdot 10^{-8}$, $4.45 \cdot 10^{-8}$ mol·cm⁻² for NP, NP/NW, and NP/NT, respectively.

Intensive research is also carried out on the use of co-adsorbents for dye solutions. As already mentioned, their function is to prevent the formation of dye aggregates on the surface of the oxide substrate. Few works, including Refs. 6 and 14, show the influence of different co-adsorbent structures on the performance of DSSCs. In the literature, in most cases, the addition of a co-adsorbent significantly improves the efficiency of the solar cell. At the same time, it is important to properly select both the type of co-adsorbent and its concentration for a particular dye. Among the works tracked, the increase in efficiency ranged from 0.24 to 1.55 percentage points [6, 12–15].

5. Conclusions

Analysing the presented results concerning the determination of the influence of the photoanode structure, including its dye sensitization method, on PV properties of the cells, the following factors can have a favourable impact on PCE: thickness of TiO₂ ca. 78 μm which is very comparable with the literature, presence of TiO₂ nanotubes as confirmed by the publications cited, use of a mixture of acetonitrile with *tert*-butanol as a dye solvent, increase of the anode immersion time in the dye solution, addition of chenodeoxycholic acid, use of phenothiazine derivatives with dibenzothiophene and methoxybenzene end-capped groups as a dye. Furthermore, using the mixture of synthesized dyes and N719 allowed to obtain a higher PCE value than the reference cell with a 50% reduction in the amount of commercial dye.

Acknowledgement

This work was supported by the National Science Centre, grant no. UMO-2016/23/B/ST8/02045

Authors' statement

Research concept and design, E.S-B.; collection and/or assembly of data, P.G.; data analysis and interpretation, P.G. E.S-B.; writing the article, E.S-B., P.G. and A.S.; critical revision of the article, E.S-B.; final approval of article, E.S-B., A.S. and P.G.

References

- [1] Kishore Kumar, D. *et al.* Functionalized metal oxide nanoparticles for efficient dye-sensitized solar cells (DSSCs): A review. *Mater. Sci. Energy Technol.* **3**, 472–481 (2020). <https://doi.org/10.1016/j.mset.2020.03.003>
- [2] Gerischer, H., Michel-Beyerle, M. E., Rebertus, F. & Tributsch, H. Sensitization of charge injection into semiconductors with large band gap. *Electrochim. Acta* **13**, 1509–1515 (1968). [https://doi.org/10.1016/0013-4686\(68\)80076-3](https://doi.org/10.1016/0013-4686(68)80076-3)
- [3] Tsubomura, H., Matsumura, M., Nomura, Y. & Amamiya, T. Dye sensitized Zinc oxide: aqueous electrolyte: platinum photocell. *Nature* **261**, 402–403 (1976). <https://doi.org/10.1038/261402a0>
- [4] O'Regan, B. & Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353**, 737–740 (1991). <https://doi.org/10.1038/353737a0>
- [5] Ji, J.-M., Zhou, H., Eom, Y. K., Kim, C. H. & Kim, H. K. 14.2% efficiency dye-sensitized solar cells by co-sensitizing novel thieno[3,2-*b*]indole-based organic dyes with a promising porphyrin sensitizer. *Adv. Energy Mater.* **10**, 1–12 (2020). <https://doi.org/10.1002/aenm.202000124>
- [6] Gnida, P., Libera, M., Pająk, A. & Schab-Balcerzak, E. Examination of the effect of selected factors on the photovoltaic response of dye-sensitized solar cells. *Energy Fuels* **34**, 14344–14355 (2020). <https://doi.org/10.1021/acs.energyfuels.0c02188>
- [7] Selvaraj, P. *et al.* Enhancing the efficiency of transparent dye-sensitized solar cells using concentrated light. *Sol. Energy Mater. Sol. Cells* **175**, 29–34 (2018). <https://doi.org/10.1016/j.solmat.2017.10.006>
- [8] Baglio, V., Girolamo, M., Antonucci, V. & Aricò, A. S. Influence of TiO₂ film thickness on the electrochemical behaviour of dye-sensitized solar cells. *Int. J. Electrochem. Sci.* **6**, 3375–3384 (2011).
- [9] Zhang, H. *et al.* Effects of TiO₂ film thickness on photovoltaic properties of dye-sensitized solar cell and its enhanced performance by graphene combination. *Mater. Res. Bull.* **49**, 126–131 (2014). <https://doi.org/10.1016/j.materresbull.2013.08.058>
- [10] Madurai Ramakrishnan, V. *et al.* Transformation of TiO₂ nanoparticles to nanotubes by simple solvothermal route and its performance as dye-sensitized solar cell (DSSC) photoanode. *Int. J. Hydrog.* **45**, 15441–15452 (2020). <https://doi.org/10.1016/j.ijhydene.2020.04.021>
- [11] Lee, S. *et al.* Two-step sol-gel method-based TiO₂ nanoparticles with uniform morphology and size for efficient photo-energy conversion devices. *Chem. Mater.* **22**, 1958–1965 (2010). <https://doi.org/10.1021/cm902842k>
- [12] Gnida, P. *et al.* Impact of TiO₂ nanostructures on dye-sensitized solar cells performance. *Materials* **14**, 13–15 (2021). <https://doi.org/10.3390/ma14071633>
- [13] Slodek, A. *et al.* New benzo [h] quinolin-10-ol derivatives as co-sensitizers for DSSCs. *Materials* **14**, 1–19 (2021). <https://doi.org/10.3390/ma14123386>
- [14] Lee, K. M. *et al.* Efficient and stable plastic dye-sensitized solar cells based on a high light-harvesting ruthenium sensitizer. *J. Mater. Chem.* **19**, 5009–5015 (2009). <https://doi.org/10.1039/b903852c>
- [15] Kumar, V., Gupta, R. & Bansal, A. Role of chenodeoxycholic acid as co-additive in improving the efficiency of DSSCs. *Sol. Energy* **196**, 589–596 (2020). <https://doi.org/10.1016/j.solener.2019.12.034>
- [16] Ko, S. H. *et al.* Nanoforest of hydrothermally grown hierarchical ZnO nanowires for a high efficiency dye-sensitized solar cell. *Nano Lett.* **11**, 666–671 (2011). <https://doi.org/10.1021/nl1037962>
- [17] Lee, K.-M. Effects of co-adsorbate and additive on the performance of dye-sensitized solar cells: A photophysical study. *Sol. Energy Mater. Sol. Cells* **91**, 1426–1431 (2007). <https://doi.org/10.1016/j.solmat.2007.03.009>

- [18] Wang, X. *et al.* Enhanced performance of dye-sensitized solar cells based on a dual anchored diphenylpyryliene dye and N719 co-sensitization. *J. Mol. Struct.* **1206**, 127694 (2020). <https://doi.org/10.1016/j.molstruc.2020.127694>
- [19] Kula, S. *et al.* Effect of thienyl units in cyanoacrylic acid derivatives toward dye-sensitized solar cells. *J. Photochem. Photobiol. B, Biol.* **197**, 111555 (2019). <https://doi.org/10.1016/j.jphotobiol.2019.111555>
- [20] Kotowicz, S. *et al.* Photoelectrochemical and thermal characterization of aromatic hydrocarbons substituted with a dicyanovinyl unit. *Dyes. Pigm.* **180**, 108432 (2020). <https://doi.org/10.1016/j.dyepig.2020.108432>
- [21] Fabiańczyk, A. *et al.* Effect of heterocycle donor in 2-cyanoacrylic acid conjugated derivatives for DSSC applications. *Sol. Energy* **220**, 1109–1119 (2021). <https://doi.org/10.1016/j.solener.2020.08.069>
- [22] Luo, J. *et al.* Co-sensitization of dithiafulvenyl-phenothiazine based organic dyes with N719 for efficient dye-sensitized solar cells. *Electrochim. Acta* **211**, 364–374 (2016). <https://doi.org/10.1016/j.electacta.2016.05.175>
- [23] Wu, Z. S. *et al.* New organic dyes with varied arylamine donors as effective co-sensitizers for ruthenium complex N719 in dye sensitized solar cells. *J. Power Sources* **451**, 227776 (2020). <https://doi.org/10.1016/j.jpowsour.2020.227776>
- [24] Dang Quang, L. N., Kaliyamurthy, A. K. & Hao, N. H. Co-sensitization of metal based N719 and metal free D35 dyes: An effective strategy to improve the performance of DSSC. *Opt. Mater.* **111**, 110589 (2021). <https://doi.org/10.1016/j.optmat.2020.110589>
- [25] Lee, H., Kim, J., Kim, D. Y. & Seo, Y. Co-sensitization of metal free organic dyes in flexible dye sensitized solar cells. *Org. Electron.* **52**, 103–109 (2018). <https://doi.org/10.1016/j.orgel.2017.10.003>
- [26] Magne, C., Urien, M. & Pauporté, T. Enhancement of photovoltaic performances in dye-sensitized solar cells by co-sensitization with metal-free organic dyes. *RSC Adv.* **3**, 6315–6318 (2013). <https://doi.org/10.1039/c3ra41170b>
- [27] Kovash Jr., C. S., Hoefelmeyer, J. D. & Logue, B. A. TiO₂ compact layers prepared by low temperature colloidal synthesis and deposition for high performance dye-sensitized solar cells. *Electrochim. Acta* **67**, 18–23 (2012). <https://doi.org/10.1016/j.electacta.2012.01.092>
- [28] Cha, S. I. *et al.* Dye-sensitized solar cells on glass paper: TCO-free highly bendable dye-sensitized solar cells inspired by the traditional Korean door structure. *Energy Environ. Sci.* **5**, 6071–6075 (2012). <https://doi.org/10.1039/c2ee03096a>
- [29] Cataldo, F. A revision of the Gutmann donor numbers of a series of phosphoramides including TEPA. *Eur. Chem. Bull.* **4**, 92–97 (2015). <https://doi.org/10.17628/ECB.2015.4.92>
- [30] Slodek, A. *et al.* Dyes based on the D/A-acetylene linker-phenothiazine system for developing efficient dye-sensitized solar cells. *J. Mater. Chem. C* **7**, 5830–5840 (2019). <https://doi.org/10.1039/C9TC01727E>
- [31] Slodek, A. *et al.* Investigations of new phenothiazine-based compounds for dye-sensitized solar cells with theoretical insight. *Materials* **13**, 2292 (2020). <https://www.mdpi.com/1996-1944/13/10/2292>
- [32] Li, X., Wang, Y., Liu, Y. & Ge, W. Green, room-temperature, fast route for NH₄Yb₂F₇:Tm³⁺ nanoparticles and their blue upconversion luminescence properties. *Opt. Mater.* **111**, 110605 (2021). <https://doi.org/10.1016/j.optmat.2020.110605>
- [33] Li, S. *et al.* Comparative studies on the structure-performance relationships of phenothiazine-based organic dyes for dye-sensitized solar cells. *ACS Omega* **6**, 6817–6823 (2021). <https://doi.org/10.1021/acsomega.0c05887>
- [34] Zhang, C., Wang, S. & Li, Y. Phenothiazine organic dyes containing dithieno[3,2-b:2',3'-d]pyrrole (DTP) units for dye-sensitized solar cells. *Sol. Energy* **157**, 94–102 (2017). <https://doi.org/10.1016/j.solener.2017.08.012>
- [35] Duvva, N., Eom, Y. K., Reddy, G., Schanze, K. S. & Giribabu, L. Bulky phenanthroimidazole-phenothiazine D- π -A based organic sensitizers for application in efficient dye-sensitized solar cells. *ACS Appl. Energy Mater.* **3**, 6758–6767 (2020). <https://doi.org/10.1021/acsaem.0c00892>
- [36] Huang, Z.-S., Meier, H. & Cao, D. Phenothiazine-based dyes for efficient dye-sensitized solar cells. *J. Mater. Chem. C* **4**, 2404–2426 (2016). <https://doi.org/10.1039/c5tc04418a>
- [37] Althagafi, I. & El-Metwaly, N. Enhancement of dye-sensitized solar cell efficiency through co-sensitization of thiophene-based organic compounds and metal-based N-719. *Arab. J. Chem.* **14**, 103080 (2021). <https://doi.org/10.1016/j.arabjch.2021.103080>
- [38] Wu, Z., Wei, Y., An, Z., Chen, X. & Chen, P. Co-sensitization of N719 with an organic dye for dye-sensitized solar cells application. *Bull. Korean Chem. Soc.* **35**, 1449–1454 (2014). <https://doi.org/10.5012/bkcs.2014.35.5.1449>
- [39] Xu, Z. *et al.* DFT/TD-DFT study of novel T shaped phenothiazine-based organic dyes for dye-sensitized solar cells applications. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **212**, 272–280 (2019). <https://doi.org/10.1016/j.saa.2019.01.002>
- [40] Afolabi, S. O. *et al.* Design and theoretical study of phenothiazine-based low bandgap dye derivatives as sensitizers in molecular photovoltaics. *Opt. Quantum Electron.* **52**, 1–18 (2020). <https://doi.org/10.1007/s11082-020-02600-5>
- [41] Arunkumar, A., Shanavas, S. & Anbarasan, P. M. First-principles study of efficient phenothiazine-based D- π -A organic sensitizers with various spacers for DSSCs. *J. Comput. Electron.* **17**, 1410–1420 (2018). <https://doi.org/10.1007/s10825-018-1226-5>
- [42] Nath, N. C. D., Lee, H. J. Choi, W.-Y. & Lee, J.-J. Electrochemical approach to enhance the open-circuit voltage (Voc) of dye-sensitized solar cells (DSSCs). *Electrochim. Acta* **109**, 39–45 (2013). <https://doi.org/10.1016/j.electacta.2013.07.057>