Baku State University: Journal of Physics & Space Sciences, **2025**, v2 (4), p. 79-89

journal homepage: http://bsuj.bsu.edu.az/en

Integrated TiO_2 nanotube DSSC–Supercapacitor platform for solar-to-hydrogen systems

Shikhamir O. Eminov[*1], Rauf H. Gardashov[2], Samira Kh. Abdullayeva[1], Ilgar I. Gurbanov[1], Elchin M. Akbarov[1], Maarif A. Jafarov[3]

[1]Institute of Physics, Ministry of Science and Education Republic of Azerbaijan, Baku, Azerbaijan
[2]Institute of Geography, Ministry of Science and Education Republic of Azerbaijan, Baku, Azerbaijan
[3]Baku State University, Department of Chemical physics of nanomaterials, Baku, Azerbaijan
Received 08-Oct-2025; Accepted 28-Nov-2025
DOİ: https://doi.org/10.30546/209501.101.2025.2.04.0134

Abstract

Integrated energy systems that combine solar energy harvesting, storage, and conversion into chemical fuels offer a promising pathway toward compact and autonomous renewable technologies. In this work, a transparent, double-sided Glass/ITO/TiO_2 nanotube (GIT) architecture is developed as a unified materials platform for integrating a dye-sensitized solar cell (DSSC), a supercapacitor , and a photoelectrochemical (PEC) water-splitting unit.

Highly ordered TiO_2 nanotube arrays were fabricated via anodization of magnetron-sputtered Ti films on ITO-coated glass substrates, followed by thermal annealing to obtain the anatase phase and RF nitrogen plasma treatment to tailor surface and electronic properties. Structural and morphological analyses (SEM, Raman spectroscopy and XRD) confirm the formation of vertically aligned crystalline nanotube arrays, while optical measurements reveal high transparency in the visible region.

The architecture incorporates a shared transparent electrode that enables direct coupling between energy harvesting and storage components, forming a compact photocharging configuration. A system-level strategy is introduced to address the intrinsic voltage mismatch between DSSC output and electrochemical processes. PEC measurements demonstrate stable photocurrent response and hydrogen evolution under ultraviolet illumination, confirming the intrinsic photoactivity of the TiO_2 nanotube electrodes. Although full device-level performance is beyond the scope of this study, the results establish a robust materials

[*]*Corresponding author* – Tel.: (+994) 50 340 34 53
e-mail: shikhamirem@gmail.com; *ORCID ID*: 0000-0002-4589-0452

and design framework for future integrated solar-to-hydrogen systems.

Keywords: Dye-sensitized solar cell (DSSC); TiO_2 nanotubes; Supercapacitor; Photoelectrochemical (PEC) conversion; Hybrid energy system.
PACS Numbers: 82.47.Uv; 81.07.De; 88.40.H.

1. Introduction

The increasing demand for clean, affordable, and sustainable energy has driven rapid progress in solar technologies capable of not only harvesting but also storing and converting energy. Integrated systems are particularly attractive for low-power applications such as portable electronics, remote sensors, and autonomous devices. Among available approaches, photovoltaic energy conversion and photoelectrochemical (PEC) water splitting are widely recognized as key components of next-generation energy technologies [1-3].

Titanium dioxide (TiO_2) is extensively studied due to its chemical stability, low toxicity, and favorable photoelectrochemical properties [4-11]. In particular, TiO_2 nanotube arrays provide a highly ordered structure with large specific surface area and efficient charge transport pathways, making them suitable for dye-sensitized solar cells (DSSCs) [12,13] supercapacitors[14-21] and PEC systems[23-25].

Previously, ordered TiO_2 nanotube layers were fabricated on ITO-coated glass via anodization of magnetron-deposited Ti films [18], resulting in transparent structures with promising structural and optical properties. The nanotubular morphology provides abundant active sites for charge storage and supports long-term stability. However, the wide bandgap of anatase TiO_2 (~3.2 eV) limits absorption primarily to the ultraviolet region. Surface modification techniques, including nitrogen plasma treatment [26], can introduce defect states and alter the electronic structure, potentially enhancing light absorption and charge carrier dynamics.

In this work, a unified architecture is proposed that integrates DSSC, supercapacitor, and PEC functionalities within a single system. Unlike conventional approaches that employ different materials for each subsystem, the present design utilizes TiO_2 nanotube arrays as a common material platform, ensuring structural compatibility and simplifying fabrication.

2. Experimental

2.1 Device Design

The conceptual architecture of the hybrid system is shown in Fig. 1. A double-sided Glass/ITO/TiO_2 nanotube (GIT) structure enables integration of a DSSC and a supercapacitor on opposite sides of a shared transparent electrode. A key challenge

is the voltage mismatch between DSSC output (~0.4–0.8 V) and the voltage required for electrochemical processes (~1.5–2.0 V). To address this, a boost converter is introduced at the system level. The DSSC consists of a TiO_2 nanotube photoanode, iodine-based electrolyte, and platinum counter electrode. The supercapacitor is formed using two TiO_2 nanotube electrodes with KOH electrolyte. The PEC unit is connected externally to demonstrate compatibility.

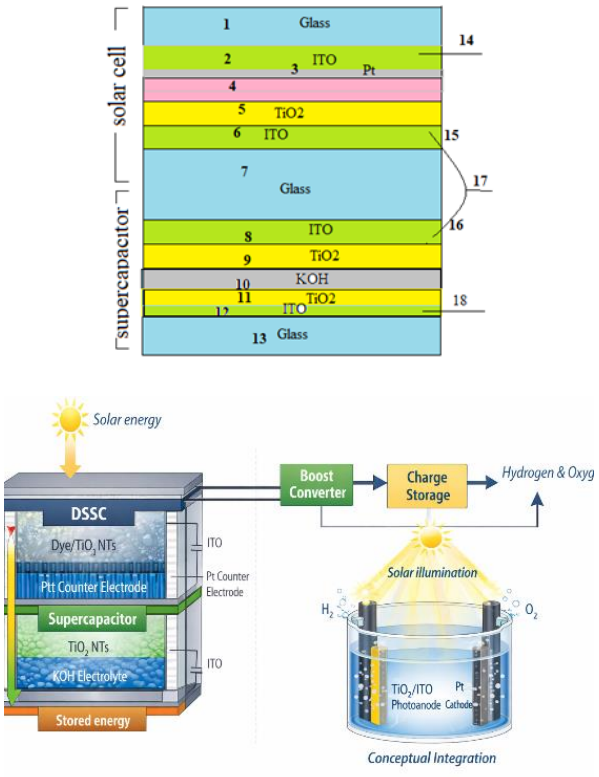

Fig. 1. Conceptual schematic of the integrated DSSC–supercapacitor platform coupled with a PEC water-splitting system for solar-driven hydrogen generation. Components: (1) top glass substrate; (2) ITO layer; (3) Pt counter electrode; (4) iodine-based electrolyte; (5) TiO_2 nanotube photoanode; (6–8, 12) ITO layers; (9, 11) TiO_2 nanotube electrodes (SC); (10) KOH electrolyte; (13) bottom glass substrate; (14–18) electrical contacts.

It should be emphasized that the schematic shown in Fig. 1 represents a conceptual integration of functional components and illustrates the energy flow within the hybrid platform. It is not intended to depict a fully optimized or experimentally validated end-to-end solar-to-hydrogen system. Rather, it highlights the architectural compatibility and material-level integration enabled by the proposed GIT platform.

A key advantage of this approach is the use of a common TiO_2 nanotube-based electrode platform, which ensures material uniformity and facilitates integration across photovoltaic, storage and PEC subsystems.

2.2 Preparation of Components

Glass substrates were cleaned and coated with ITO and Ti using magnetron sputtering. The Ti films were anodized in ethylene glycol electrolyte to form TiO_2 nanotubes.

Samples were annealed at 450°C to obtain anatase phase, followed by RF nitrogen plasma treatment to modify electronic and surface properties.

2.3 Characterization

SEM, XRD, Raman spectroscopy, and UV–Vis spectroscopy were used to analyze morphology, structure, and optical properties of the films. PEC activity was evaluated using TiO_2 nanotubes formed on titanium foil for improved electrical contact.

3. Results and Discussion

3.1. Structural, morphological and optical properties of NT TiO_2

The structural, morphological, optical, and photo electrochemical properties of the fabricated TiO_2 nanotube-based system were systematically investigated to evaluate its suitability as a common materials platform for integrated DSSC, supercapacitor, and PEC components.

SEM analysis (Figure 2) confirms vertically aligned TiO_2 nanotube arrays with diameters of ~ 150 nm and thickness ~3 μm. The structure is uniform and highly ordered. Such morphology provides a high specific surface area and facilitates efficient charge transport pathways, which are essential for multifunctional applications including photovoltaic conversion, charge storage, and photoelectrochemical processes.

The optical transmittance spectra of the multilayer GIT structure are presented in Fig. 3. In the visible region (400–750 nm), the films exhibit high transparency with interference fringes arising from multiple reflections at the interfaces. This high optical transparency is critical for front-side illumination in DSSC configurations and supports the feasibility of the proposed integrated platform.

The optical band gap of the TiO_2 thin film was determined from the **transmission spectra** using the Tauc relation: $\alpha h\upsilon \propto B(h\upsilon - E_g)^2$. As shown in Fig. 4 the $(\alpha h\upsilon)^{1/2}, [\mathrm{cm}^{-1/2}\mathrm{eV}^{1/2}]$ versus hν plot exhibits a linear region near the absorption edge, indicating a direct allowed transition. Extrapolation of this linear portion to

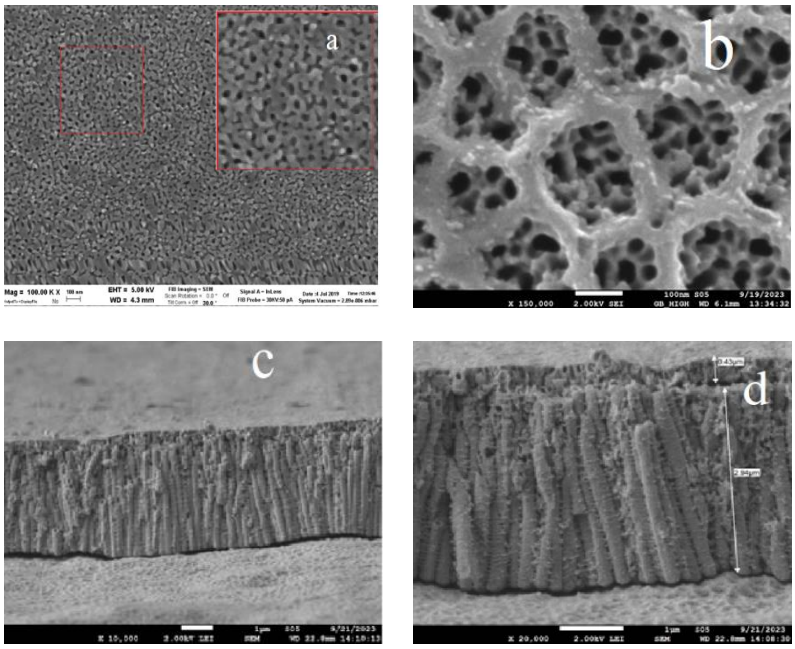

Fig. 2. SEM images of TiO_2 nanotube arrays: (a, b) top-view images showing surface morphology; (c, d) cross-sectional views demonstrating vertically aligned nanotube structure.

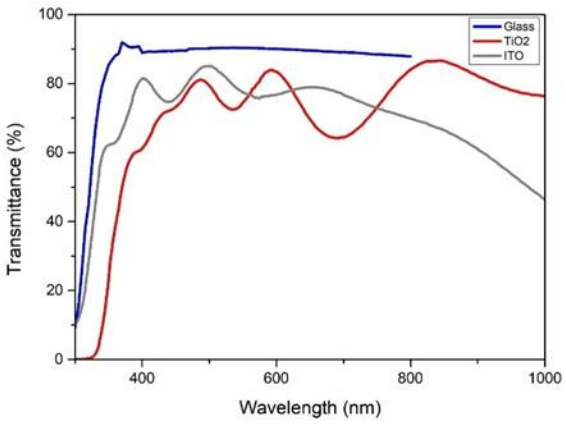

Fig. 3. Optical transmittance spectra of the Glass/ITO/TiO_2 structure and individual layers in the visible spectral range.

the energy axis yields a band gap of $E_9 \approx 3.2$ eV. A sub-bandgap absorption feature in the 2.75–3.00 eV range is observed prior to the main edge. This is attributed to defect-related states (oxygen vacancies V_O^- and Ti^{3+} centers) and surface states, which introduce intermediate energy levels enabling additional optical transitions.

The nanotubular structure also contributes to band tailing (Urbach tail), enhancing absorption at lower photon energies. These results, obtained from the transmission-based analysis of the fabricated NT-TiO_2 layers, confirm their suitability for solar energy conversion applications.

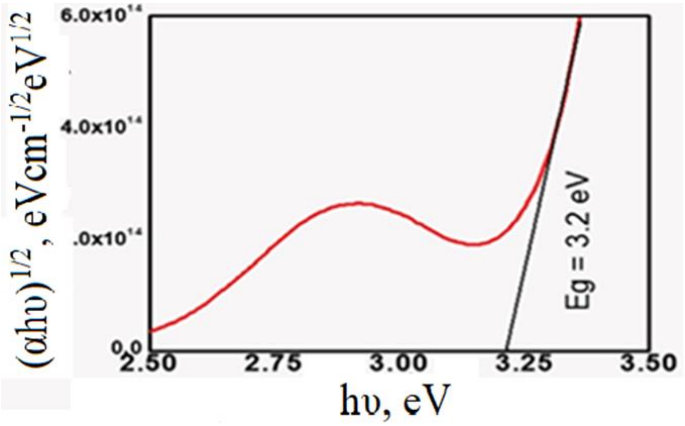

Figure 4. Optical band gap of NT-TiO_2 (Tauc plot)

Raman and XRD analyses confirm the anatase phase and good crystallinity.Raman spectroscopy results (Fig. 5) reveal characteristic vibrational modes at 143, 197, 339, 391, 513, 519, and 639 cm^{-1}, which are consistent with the anatase phase of TiO_2 [27,28]. The presence of well-defined Raman peaks indicates a crystalline structure with good phase purity.

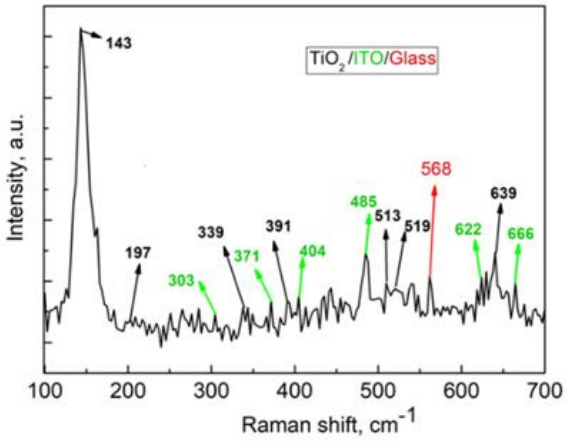

Fig. 5. Raman spectrum of the Glass/ITO/TiO_2 structure showing characteristic vibrational modes of anatase TiO_2.

The X-ray diffraction (XRD) pattern shown in Fig.6 further confirms the formation of anatase TiO_2, with diffraction peaks corresponding to the (101), (004), (200), (105), (204), and (116) crystallographic planes. These results validate the structural suitability of the TiO_2 nanotube layers as a common material platform for integrated DSSC, supercapacitor, and PEC subsystems.

The combination of well-defined nanotube morphology, high optical transparency, and confirmed anatase crystallinity demonstrates that the fabricated GIT structure provides a robust and multifunctional materials platform for integrated solar energy systems.

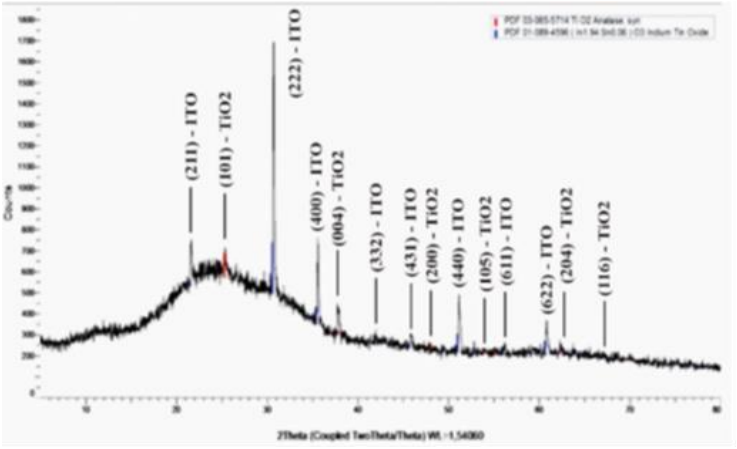

Fig. 6. X-ray diffraction pattern of the Glass/ITO/TiO_2 structure confirming the formation of anatase TiO_2.

3.2. Photoelectrochemical validation of TiO_2 nanotube material

To further assess the intrinsic photoelectrochemical activity of the TiO_2 nanotube material, independent of substrate-related limitations, additional experiments were conducted using TiO_2 nanotube arrays directly formed on titanium foil. The resulting TiO_2 photoanode, with a geometrical area of 1.2 cm^2, provided improved electrical contact and mechanical robustness, enabling more reliable PEC measurements.

PEC experiments were carried out in a 1 M KOH electrolyte using a TiO_2 nanotube photoanode and a Pt cathode. An external bias of 1.5 V was applied, exceeding the thermodynamic potential of 1.23 V required for water splitting, in order to compensate for kinetic overpotentials and interfacial losses. Ultraviolet illumination was supplied by a high-pressure mercury–quartz arc lamp (DRS-250) with an estimated power density of ~50 $mW \cdot cm^{-2}$. The emission spectrum of the lamp is dominated by a strong line at 365 nm, which closely matches the band gap energy of

TiO_2 (~3.2 eV), enabling efficient photogeneration of electron–hole pairs.

Under UV illumination (~365 nm), the photocurrent increased from 0.06 mA in the dark to 0.20 mA, corresponding to a photocurrent density of ~0.15 $mA \cdot cm^{-2}$. Based on Faraday's law of electrolysis, the hydrogen evolution rate was estimated to be approximately 8×10^{-6} $mol \cdot h^{-1}$ (~0.063 $mL \cdot h^{-1}$). These results confirm that the TiO_2 nanotube architecture effectively supports charge separation and participates in photoelectrochemical reactions leading to hydrogen evolution. The obtained photocurrent density is consistent with reported values [6-9] for undoped TiO_2 photoelectrodes, where performance is typically constrained by the wide band gap, rapid charge recombination, and sluggish interfacial kinetics. Importantly, these results validate the intrinsic PEC functionality of the TiO_2 nanotube material employed in the integrated system, rather than being limited by substrate effects.

Although the observed photocurrent and hydrogen evolution rates remain relatively modest, this behavior reflects the inherent limitations of pristine TiO_2, including restricted visible-light absorption and recombination losses. Nevertheless, the stable and reproducible photoresponse demonstrates that the material is functionally active and provides a reliable platform for further optimization.

These findings indicate that targeted material modification strategies—such as doping, surface passivation, cocatalyst deposition, or bandgap engineering—could significantly enhance PEC performance. In particular, achieving photocurrent densities in the range of 0.5–1 $mA \cdot cm^{-2}$ appears feasible and is consistent with values reported for modified TiO_2-based systems.

4. Conclusion

A transparent, double-sided Glass/ITO/TiO_2 nanotube (GIT) platform was developed to integrate solar energy harvesting, storage, and PEC conversion. Highly ordered anatase TiO_2 nanotube arrays were fabricated on ITO-coated glass via anodization of magnetron-deposited Ti films, followed by thermal annealing and nitrogen plasma treatment, yielding vertically aligned nanostructures with high optical transparency and well-defined crystallinity. The design enables a dye-sensitized solar cell and a supercapacitor to share a single transparent electrode, forming a compact photocharging configuration, while a system-level approach addresses the intrinsic voltage mismatch between photovoltaic output and electrochemical processes, facilitating coupling with a PEC water-splitting unit. Although full device-level operation has yet to be demonstrated, this study establishes a robust materials and structural foundation for integrated DSSC-supercapacitor-PEC systems. Future work will focus on optimizing photovoltaic performance, charge storage, and hydrogen generation efficiency to realize fully integrated, self-powered solar-to-hydrogen devices on a single material platform.

Acknowledgments: During the preparation of this work, the authors used ChatGPT (OpenAI) to assist in organizing the manuscript, compiling background information, and improving the English language. All experimental work, data, and scientific concepts reported in this manuscript are original and were independently developed and carried out by the authors. After using this tool, the authors critically reviewed and edited the content and take full responsibility for the accuracy and integrity of the publication.

Declarations. The authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Sharma L, Kamlesh S, Jain K, Sharma A. Solar cells: in research and applications—a review. Materials Sciences and Applications. 2015;6:1145–1155. DOI: 10.4236/msa.2015.612113

[2] Askari MB, Mirzaei MA, Mirhabibi M. Types of solar cells and application. Am J Opt Photonics. 2015;3(5):94–113. DOI: 10.11648/j.ajop.20150305.17

[3] Gardashov E., Eminov M., Kara G, Gardashov R. Simulation and visualizations of solar car motion along the road. J Atmos Sol Terr Phys. 2025;271:106524. https://doi.org/10.1007/978-1-4614-6431-0_182-1

[4] Rahimli, A., Huseynova, A., Alekberov, R., & Jafarov, M. (2025). Optimizing thermal stability and structural integrity in polystyrene nanocomposites with rutile TiO_2 nanoparticles. Ceramics International. https://doi.org/10.1016/j.ceramint.2025.01.016

[5] Hajiyeva, F. V., Rahimli, A. M. Influence of polarization charges on the photoluminescence properties of nanocomposites based on polyvinylidene fluoride and titanium dioxide nanoparticles. J. Inorg. Organomet. Polym. Mater. 2017, NS1, 239-243. https://doi.org/10.1007/s10904-017-0675-9

[6] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972;238:37–38. DOI: 10.1038/238037a0

[7] Fajrina N, Tahir M. A critical review in strategies to improve photocatalytic water splitting towards hydrogen production. Int J Hydrogen Energy. 2019;44:540–538. DOI: 10.1016/j.ijhydene.2018.10.200

[8] Wang S, Lu A, Zhong CJ. Hydrogen production from water electrolysis: role of catalysts. Nano Convergence. 2021;8:4. DOI: 10.1186/s40580-021-00254-x

[9] Rafique MM, Hajra S, Irshad M, et al. Hydrogen production using TiO_2-based photocatalysts: a comprehensive review. ACS Omega. 2023;8(29):25640–25649. DOI: 10.1021/acsomega.3c00963

[10] Al-Mamun MR, Kader S, Islam MS, Khan MZH. Photocatalytic activity improvement and

application of UV-TiO_2 photocatalysis in textile wastewater treatment: a review. J Environ Chem Eng. 2019;7(5):1032488. DOI: 10.1016/j.jece.2019.103248

[11] Liu X, Hua R, Niu J, Zhang Z, Zhang J. N_2 plasma treatment TiO_2 nanosheets for enhanced visible light-driven photocatalysis. J Alloys Compd. 2021;881:160509. https://doi.org/10.1016/j.jallcom.2021.160509

[12] Grätzel M. Photoelectrochemical cells. Nature. 2001;414(6861):338–344.

doi:10.1038/35104607 DOI: 10.1038/35104607

[13] Grätzel M. Recent advances in sensitized mesoscopic solar cells. Acc Chem Res. 2009;42(11):1788–1798. DOI: 10.1021/ar900141y

[14] Abdullayeva S, Eminov S, et al. Synthesis of anodic TiO_2 nanotubes on indium tin oxide coated glass electrodes. Int J Energy Res. 2022;46(10):14558–14570.

https://doi.org/10.1002/er.8667

[15] Elshahawy AM, Elkatlawy SM, Shalaby MS, et al. Surface-engineered TiO_2 for high-performance flexible supercapacitor applications. J Electron Mater. 2023;52:1347–1357. https://doi.org/10.1007/S11664-022-10084-0

[16] Ahmed F, Syed A, Pervez SA, Aljaafari A, et al. Fabrication of TiO_2-nanotube-array-based supercapacitors. Micromachines. 2019; 10(11): 742.

https://doi.org/10.3390/mi10110742

[17] Dar F.I., Moonoosawmy K.R., Es-Souni M. Morphology and property control of NiO nanostructures for supercapacitor applications. Nanoscale Res Lett. 2013;8:363. https://doi.org/10.1186/1556-276X-8-363

[18] Eminov Sh, et al. Integration of electrical energy storage devices with photovoltaic solar cells in one hybrid system. In: Krishnamoorthy S, Iniewski K, eds. Advances in Fabrication and Investigation of Nanomaterials for Industrial Applications. Cham: Springer; 2024. p.353–371. DOI:10.1007/978-3-031-42700-8_18.

[19] Eminov Sh, Tagiyev D, Aliyev A, Jalilova K, Guliyev J, et al. Integration of supercapacitor with solar cell based on NiO and CdS nanopillars embedded in porous anodic alumina templates. Int J Energy Res. 2022;1–11. DOI:10.1002/er.8741

[20] Nordin NA, Ansari M, Nomanbhay SM. Integrating photovoltaic (PV) solar cells and supercapacitors for sustainable energy devices: a review. Energies. 2021;14:7211. https://doi.org/10.3390/en14217211

[21] Zhang Q, Li G, Qiao F. Recent advances in integrated solar cell/supercapacitor devices: fabrication, strategy and perspectives. J Adv Res. 2025;67:197–219. DOI: 10.1016/j.jare.2024.01.032

[22] Mizukoshi Y, Ohtsu N, Semboshi S, Masahashi N. Visible light responses of sulfur-doped rutile titanium dioxide photocatalysts fabricated by anodic oxidation. J Photochem Photobiol A Chem. 2019;91(1–2):152–155.

https://doi.org/10.1016/j.apcatb.2009.05.018

[23] Ge M, Cai J, Iocozzia J, Cao C, et al. A review of TiO_2 nanostructured catalysts for sustainable H_2 generation. Int J Hydrogen Energy. 2017;42:8418–8449.
https://doi.org/10.1016/j.ijhydene.2016.12.052

[24] Sevinj G. Nuriyeva, Aynura H. Karimova, Flora V. Hajiyeva Structural and Optical Behavior of Commercial vs. Synthesized ZnO Nanoparticles Doped with Europium via Wet Impregnation / Journal of Physics & Space Sciences, 2025, v2(3) 20250203 63-77 https://doi.org/10.30546/209501.101.2025.2.03.032

[25] Qian F, Tian J, Bai Z, Liu L, Cao M, Li J, Chen S. $CoNi_2S_4$ cocatalyst modified TiO_2 nanorods/nanoflower homojunction for efficient photoelectrochemical water splitting. J Alloys Compd. 2024;991:174567. https://doi.org/10.1016/j.jallcom.2024.174567

[26] Pulsipher DJ, Martin IT, Fisher ER. Controlled nitrogen doping and film colorimetrics in porous TiO2 materials using plasma processing. ACS Appl Mater Interfaces. 2010 Jun;2(6):1743-53. doi: 10.1021/am100233j. PMID: 20527731

[27] Ekoi EJ, Gowen A, Dorrepaal R, Dowling DP. Characterization of titanium oxide layers using Raman spectroscopy and optical profilometry: influence of oxide properties. Results Phys. 2019;12:1574–1585. https://doi.org/10.1016/j.rinp.2019.01.054

[28] Hardcastle FD. Raman spectroscopy of titania (TiO_2) nanotubular water-splitting catalysts. J Ark Acad Sci. 2011;65:43–46. https://doi.org/10.54119/jaas.2011.6504.