

THE EFFECT OF RED AND YELLOW CARBON QUANTUM DOTS (CQDS) IN TiO_2 PHOTOANODES FOR DSSC APPLICATION

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ABSTRACT

The exploration of Dye-Sensitized Solar Cells (DSSC), especially regarding the photoanode, is steadily advancing. Widely recognized, the photoanode plays a key role in absorbing light and facilitating electron generation, which is essential for the efficiency of Dye-Sensitized Solar Cells (DSSC). TiO_2 is frequently used as photoanode due to its excellent stability and ability to effectively support dye molecules. However, in terms of enhancing light absorption and the electron transfer rate, doping with Carbon Quantum Dots (CQDs) in TiO_2 -based photoanodes has gained attention as a promising approach to improve efficiency. In this research, Carbon Quantum Dots (CQDs) were added to TiO_2 to enhance its properties. Red CQDs and Yellow CQDs were incorporated into TiO_2 at a concentration of 5%. The resulting composite materials were characterized using XRD, UV-Vis, and I-V measurements with a solar simulator. The XRD pattern confirmed the crystalline structure of TiO_2 with incorporated CQDs. The optical properties of the CQD- TiO_2 composites were analyzed through UV-Vis spectroscopy, revealing changes in light absorption. The DSSC performance parameters, including J_{sc} , V_{oc} , FF , and η , were determined through I-V characterization using a solar simulator. The best DSSC performance was obtained by the sample with the addition of 5% Yellow CQDs, with an efficiency of 3.42%

Keywords: CQDs; TiO_2 ; Photoanode; DSSC

Introduction

Nowadays, the development of renewable energy is becoming very rapid, and solar cells will play an important role as an environmentally friendly and low-cost electricity supply.¹ Dye Sensitized Solar Cell (DSSC) is one of the practical and effective third-generation solar cells for future energy supply.² DSSC was declared a great success by O'Regan and Grätzel in 1991 and is the only type of solar cell based on organic material.³ In addition, DSSC has several advantages, such as its easy, environmentally friendly, and inexpensive manufacturing process.⁴ In general, DSSC is assembled with a unique sandwich structure with four main components, namely photoanode, dye sensitizer, redox electrolyte and counter electrode.⁵

Photoanodes are an important component of DSSC because they have photoabsorption capabilities that allow for high efficiency and energy conversion.⁶ In DSSC, the photoanode must have a large surface area to absorb the dye molecules, rapid electron migration and band gap energy which is ideal for effective photoactive electron injection.^{7,8} The photoanode itself consists of an FTO glass substrate with a thin layer of semiconductor material.⁴

The most widely used semiconductor material is titanium dioxide (TiO_2). TiO_2 is a dioxide-transition metal with a band gap of 3.2 eV.⁹ TiO_2 is the most widely used semiconductor material for DSSC, due to its chemically and thermally stable, cost-effective, and non-toxic properties.¹⁰ However, it is known that TiO_2 has slow electron mobility ($30 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$) and low dye

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adsorption thus limiting the further efficiency gains of TiO_2 -based DSSC.^{11,12}

On the other hand, quantum dot (QDs)-based DSSCs have shown promising performance to overcome this problem in order to achieve high photoconversion stability and efficiency.¹³ In this case, carbon QDs modified photoanodes (CQDs) for DSSC applications show low recombination rates, increased dye adsorption, and rapid electron transport in devices.¹⁴ In addition, due to its fast electron transfer time (<15 fs from CQDs to TiO_2), long electron lifetime (about 100 ps), low cost, and outstanding biocompatibility.¹⁵

CQDs are generally quasi-spherical in shape and consist of amorphous or crystalline carbon.¹⁶ Several core models of CQDs have been proposed in recent years, including diamond-like structures, graphite/oxide structures, and amorphous carbon structures.¹⁷ CQDs absorb light primarily in the ultraviolet (UV) range (260–320 nm), with some absorption continuing to visible wavelengths.¹⁸ CQDs have the dual effect that nanoparticles have in photocatalytic systems, leading to their great potential for high-performance photocatalyst designs.¹⁹ CQDs exhibit the absorption behavior of electrons in ultraviolet (UV), which is useful for capturing scattered electrons produced by metal oxides. CQDs and various bulk semiconductors have been combined to seek the best modification of the optical properties of composite materials such as TiO_2 .

Methods

The method carried out refers to the research of Pujiarti et al.²⁰ TiO_2 photoanode is made by coating Titanium BL-1 which is used as a blocking layer using the spin coating method at a speed of 3000 rpm for 1 minute, heated gradually, at a temperature of 100°C for 15 minutes, 300°C for 15 minutes, and 500°C for 30 minutes. TiO_2 T/SP is doped with CQDs. After that, it is depositioned using the screen printing method, then heated with a hot plate of 100°C to a temperature of 500°C with a temperature increase of 100°C every 10 minutes with a peak temperature of 30

minutes. In the same way the subsequent deposition of the TiO_2 R/SP layer.

The DSSC system is composed of photoanode parts immersed in a 0.7 mM dye N719 solution for 24 hours in a dark room with room temperature. Furthermore, the area that is not an active area, is given surlyn, then added with a Pt-counter electrode and a sealing process is carried out with the help of a hot press. After that, iodine electrolyte injection is carried out under vacuum conditions.

TiO_2 /CQDS samples will be characterized using XRD, UV-Vis and I-V spectroscopy. The tool to be used for XRD characterization is XRD PanAnalytical type X'Pert pro, the beam used in the XRD tool is Cu $\text{K}\alpha$ which has a wavelength of 1.540589 Å. UV-Vis used is the Analytik Jena Specord 200 plus brand. The tool used for I-V characterization is the Keithley 2400 type I-V electrometer. Result and Discussion

Table 1. Sample Code

No.	Sample	Details
1.	TC-0	TiO_2 + 0% CQDs
2.	TC-5R	TiO_2 + 5% Red CQDs
3.	TC-5Y	TiO_2 + 5% Yellow CQDs

Structure Analysis

Based on the XRD results in Figure 1. The peak of TiO_2 doping CQDs was identified at the diffraction angle (2θ) of 25.36° and 25.44° while the main peak of TiO_2 without doping at the diffraction angle (2θ) was 25.57°. The shift in the diffraction peak is due to the addition of CQDs doping. The results of the TiO_2 peak have been in accordance with the research that has been conducted by Bakr et al.²¹

The crystal size of the TiO_2 /CQDs photoanode is shown in Table 2. The results showed that the photoanode crystal sizes were 37.58, 46.96, and 27.11 nm, respectively. In DSSC, the small crystal size results in a larger surface area, thereby increasing light absorption and electron collection.²² The higher surface area causes dye particles to be attached, which results in higher efficiency for DSSC.²³



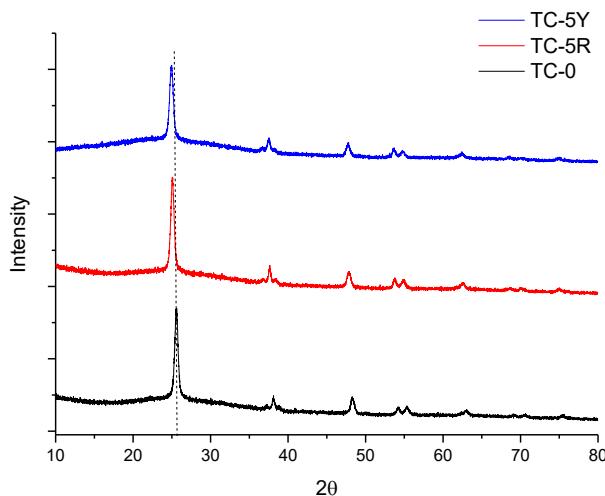


Figure 1. X-Ray Diffraction Patterns

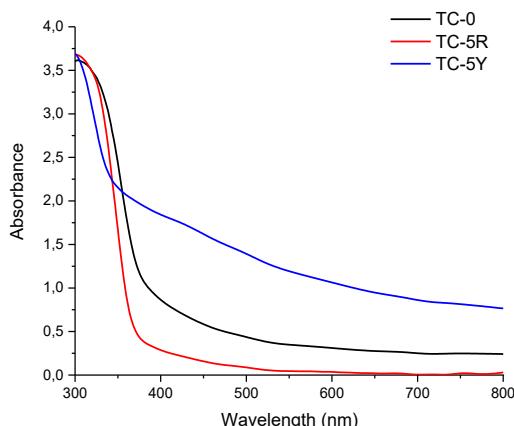
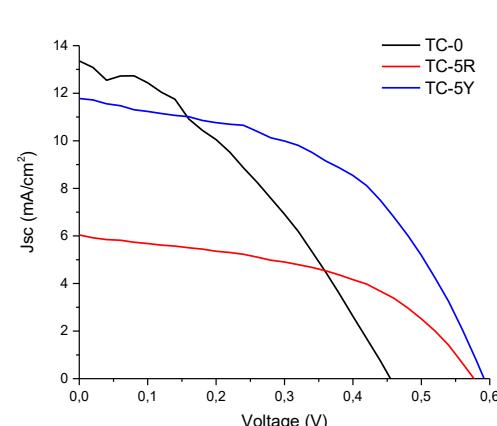
Figure 3. J-V Curve DSSC TiO₂/CQDsFigure 2. Absorbance DSSC TiO₂/CQDs

Table 2. Photoanode crystal size

No.	Sample	2 theta (2θ)	FWHM	Crystal Size (nm)
1.	TC-0	25,57	0,21	37,58
2.	TC-5R	25,36	0,17	46,96
3.	TC-5Y	25,44	0,31	27,11

UV-Vis Spectra

The optical properties and ultraviolet absorption of TiO₂/CQDs photoanodes were studied through UV-Vis characterization in the wavelength range of 300-800 nm. Figure 2 shows the photoanode absorbance spectra of TiO₂/CQDs. It can be seen that the maximum absorption region of TiO₂/CQDs photoanodes

for all variations is at the peak of absorption around 300-350 nm. The TC-5Y sample has a larger absorption area than the other samples. This indicates that more energy will be absorbed from light. The absorption spectrum extends to the high-wavelength region due to some low-energy transitions that occur in the functional groups present on the surface of CQDs.¹



Table 3. Photovoltaic Parameters TiO_2/CQDs

No.	Sampel	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
1.	TC-0	13.36	0.45	0.35	2.14
2.	TC-5R	6.04	0,58	0,48	1,67
3.	TC-5Y	11.78	059	0,49	3.42

Performance

The DSSC photovoltaic parameters are shown in Table 2. Based on the performance test results, the highest efficiency of 3.42% was obtained for TC-5Y with J_{sc} and V_{oc} of 11.78 mA/cm² and 0.58 V. One of the most important factors affecting the conversion efficiency of solar cells is effective charge separation, increased electron transfer rate, and reduction of the recombination process.²⁴ Doping CQDs increases the effectiveness of well-transferred electrons to the TiO_2 conduction band and holes accumulated in the valence band of CQDs. The presence of CQDs nanostructures in CQDs/ TiO_2 leads to a shift in Fermi levels to higher levels, and the result is that the V_{oc} for CQDs/ TiO_2 modified photoanodes is increased compared to pure TiO_2 .²⁴

Conclusion

TiO_2/CQDs photoanodes with CQDs-Yellow doping of 5% have better performance than pure TiO_2 with one of the main factors in the improvement being the effectiveness of electron transfer and reduced electron recombination. The XRD results showed that the smallest crystal size obtained from TC-5Y was 27.11 nm which resulted in an increase in the optimal surface area for photon absorption. UV-Vis characterization showed that the TC-5Y sample had a larger long absorption area than other samples. The best DSSC photovoltaic performance obtained was 3.42% by the TC-5Y.

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References

1. R. H. Althomali et al.. A novel Pt-free counter electrode based on MoSe₂ for cost effective dye-sensitized solar cells (DSSCs): Effect of Ni doping. *Journal of Physics and Chemistry of Solids*. Nov. 2023;182:p.111597
2. H. T. Weldemicheal, M. A. Desta, and Y. S. Mekonnen. Derivatized photosensitizer for an improved performance of the dye-sensitized solar cell. *Results in Chemistry*. Jan. 2023;5: p. 100838
3. Arka, Girija Nandan; Prasad, Shashi Bhushan; Singh, Subhash. Comprehensive study on dye sensitized solar cell in subsystem level to excel performance potential: A review. *Solar Energy*. 2021; 226: 192-213.
4. Magiswaran, Kaiswariah, et al. Controlling the Layer Thickness of Zinc Oxide Photoanode and the Dye-Soaking Time for an Optimal-Efficiency Dye-Sensitized Solar Cell. *Coatings*. 2022; 13(1): 20.
5. Teng, Genhui, et al. Strategic design of self-generated Ni-NC hybrid sites in 3D network structures as counter electrodes in photovoltaics. *Resources Chemicals and Materials*. 2023; 2(1): 1-10.
6. Kumar, Yogesh, et al. Photoanode modified with nanostructures for efficiency enhancement in DSSC: a review. *Carbon Letters*. 2023; 33(1): 35-58.
7. Chinnarani, M.; Prabu, K. M.; Suresh, S. Plasmonic silver loaded anatase titanium dioxide nanospheres photoanode for dye-sensitized solar cell. *Results in Chemistry*. 2023; 5: 100835.



8. Pandian, S. Alex; Sivakumar, M. Barium titanate perovskite nanoparticles integrated reduced graphene oxide nanocomposite photoanode for high performance dye-sensitized solar cell. *Results in Chemistry*. 2023; 6: 101091.
9. Ramaripa, Phuti S., et al. Influence of phthalocyanine nanowire dye on the performance of titanium dioxide-metal organic framework nanocomposite for dye-sensitized solar cells. *Chemical Engineering Journal Advances*. 2023; 14: 100485.
10. Nizamudeen, C., et al. Photovoltaic performance of MOF-derived transition metal doped titania-based photoanodes for DSSCs. *Scientific reports*. 2023; 13(1): 6345.
11. Kouhestanian, Elham, et al. Enhancing the electron transfer process of TiO₂-based DSSC using DC magnetron sputtered ZnO as an efficient alternative for blocking layer. *Organic Electronics*. 2020; 86: 105915.
12. Xie, Fengyan, et al. One-step synthesis of hierarchical SnO₂/TiO₂ composite hollow microspheres as an efficient scattering layer for dye-sensitized solar cells. *Electrochimica Acta*. 2019; 296: 142-148.
13. Shejale, Kiran P., et al. Nitrogen doped carbon quantum dots as Co-active materials for highly efficient dye sensitized solar cells. *Carbon*. 2021; 183: 169-175.
14. Cheruku, Rajesh, et al. Photo-electrodes decorated with carbon quantum dots: Efficient dye-sensitized solar cells. *Results in Engineering*. 2023; 20: 101611.
15. Huang, Ping, et al. Carbon quantum dots improving photovoltaic performance of CdS quantum dot-sensitized solar cells. *Optical Materials*. 2020; 110: 110535.
16. Jorns, Mychele; Pappas, Dimitri. A review of fluorescent carbon dots, their synthesis, physical and chemical characteristics, and applications. *Nanomaterials*. 2021; 11(6): 1448.
17. Khan, Mohammad Ehtisham; Mohammad, Akbar; Yoon, Taeho. State-of-the-art developments in carbon quantum dots (CQDs): Photo-catalysis, bio-imaging, and bio-sensing applications. *Chemosphere*. 2022; 302: 134815.
18. Thangaraj, Baskar; Solomon, Pravin R.; Ranganathan, Srinivasan. Synthesis of carbon quantum dots with special reference to biomass as a source-a review. *Current pharmaceutical design*. 2019; 25(13): 1455-1476.
19. Pirsahib, Meghdad, et al. Application of carbon quantum dots to increase the activity of conventional photocatalysts: A systematic review. *Journal of Molecular Liquids*. 2018; 271: 857-871.
20. Ramadhani, Dea Agnestasya Kurnia, et al. Ag-doped TiO₂ as photoanode for high performance dye sensitized solar cells. *Materials Science for Energy Technologies*. 2024; 7: 274-281.
21. Bakr, Nabeel A.; Ali, Abdulrahman K.; Jassim, Shaimaa M. Fabrication and efficiency enhancement of Z907 dye sensitized solar cell using gold nanoparticles. *Journal of Advanced Physics*. 2017; 6(3): 370-374.
22. Abdullah, N. A.; Ali, B.; Jabbar, Hashim. Study the effect of TiO₂ nanoparticles in multilayers of photoelectrode prepared by ball milling technique on the performance of dye sensitized solar cells (Dsscs). In: *Journal of Physics: Conference Series*. IOP Publishing. 2021: p. 012069.
23. Liang, Meng-Suan, et al. Studies on the effects of crystallite sizes and scattering layers on the conversion efficiency of dye-sensitized solar cell. *Journal of Power and Energy Engineering*, 2014. 2(12): 18.
24. Rezaei, Behzad, et al. The impressive effect of eco-friendly carbon dots on improving the performance of dye-sensitized solar cells. *Solar Energy*. 2019; 182: 412-419.

