



سنتز نانوذرات TiO_2 با روش سل-ژل برای ساخت سلول‌های خورشیدی حساس شده با رنگدانه طبیعی میوه جمبو

ماندانا شادکام^۱، ته‌مین جلالی^۱، محسن محرابی^۱ و شهریار عصفوری^۲

^۱گروه فیزیک دانشگاه خلیج فارس، بوشهر، ایران؛ ^۲گروه مهندسی شیمی دانشگاه خلیج فارس، بوشهر، ایران

چکیده- در این مطالعه، نانوذرات TiO_2 به منظور دستیابی به بلورینگی بالا و اندازه کوچک ذرات، به روش سل-ژل سنتز شده و سپس مشخصه‌های نانوذره‌های تهیه شده به وسیله پراش پرتو ایکس (XRD) و طیف سنج مادون قرمز (FT-IR) ارزیابی شدند. سلول خورشیدی رنگدانه‌ای با استفاده از لایه نشانی خمیر نانوذرات TiO_2 بر روی زیرلایه شیشه‌ای FTO (اکسید قلع آلاییده شده با فلورین) تحت عنوان فیلم اکسید نیمه رسانا ساخته شد. همچنین در این تحقیق، برای کاهش هزینه‌ها، از رنگدانه طبیعی استخراج شده از میوه جمبو استفاده شده است. پارامترهای فتوولتائیک تحت نور خورشید شبیه سازی شده با شدت تابش 100 mW/cm^2 و تابش استاندارد ($\text{AM}1.5$) اندازه گیری شد. نتایج نشان داد بازده تبدیل انرژی 1.36% و سایر مشخصه های فتوولتائیک شامل جریان مدار کوتاه، ولتاژ مدار باز و فاکتور پر شدن به ترتیب 5.88 mA/cm^2 ، 0.6235 V و 0.3706 می باشند.

کلید واژه- رنگدانه طبیعی، روش سل-ژل، سلول‌های خورشیدی رنگدانه‌ای، فتوآند، نانوذرات TiO_2

Synthesis of TiO_2 nanoparticles using the sol-gel method to fabricate dye-sensitized solar cells with natural Syzygium Cumini fruit dye

M. Shadkam^۱, T. Jalali^{۱*}, M. Mehrabi^۱, and S. Osfoury^۲

^۱Department of Physics, Persian Gulf University, Bushehr, Iran; ^۲Department of Chemical Engineering, Persian Gulf University, Bushehr, Iran, *jalali@pgu.ac.ir

Abstract In this study, TiO_2 nanoparticles were synthesized using the sol-gel method to obtain a highly crystalline and small particle size of TiO_2 ; the produced nanoparticles were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Dye-sensitized solar cell (DSSC) was fabricated with a layer of TiO_2 nanoparticles paste deposited on FTO (fluorine-doped tin oxide) glass substrate as a semiconductor oxide film. Also in this study, extracted natural dye from Syzygium Cumini fruit was used for decrease the cost. The photovoltaic parameters were measured using the solar simulator under an incident light intensity of 100 mW/cm^2 and air mass ($\text{AM}1.5$). The results show power conversion efficiency (η) of 1.36% and other photovoltaic parameters include short circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (FF) are 5.88 mA/cm^2 , 0.6235 V and 0.3706 respectively.

Keywords: Dye-sensitized solar cells, Natural dye; Photoanode, Sol-gel method; TiO_2 nanoparticles

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their low cost and easy fabrication with relatively high photo-conversion efficiency. O'Regan and Grätzel fabricated TiO_2 based DSSC for the first time in 1991 [1]. A typical DSSC is made up of semiconductor oxide film for attaching dye molecules, a counter electrode with deposited layer of platinum and an electrolyte solution. Sun light is absorbed by dye molecules and then electrons are injected to the conduction band of semiconductor oxide. Meanwhile oxidized dye molecules are regenerated by electrolyte solution also electrolyte ions regenerated through counter electrode. Semiconductor oxide film is the heart of DSSCs and the most studied materials are TiO_2 , ZnO and SnO_2 which TiO_2 has announced as the best one due to its unique properties and various advantages such as photochemical stability, high band gap (~ 3.2 eV), excellent optical transparency capability, availability, and non-toxicity. TiO_2 exists in three main phases, namely, rutile, anatase and brookite. However rutile phase is more thermal stable, anatase phase is the first choice for DSSCs applications due to its higher band gap energy [2, 3]. Nanocrystalline TiO_2 such as sol-gel, hydrothermal, solvothermal and etc. which sol-gel is one of the most used methods due to highly crystalline and small size of synthesized nanoparticles [4-6]. The sol-gel is a simple, fast, and cost-effective method, which has received much attention due to providing controlled grain size as well as particle morphology, achieving superior purity, compositional homogeneity, low processing temperature, and production with simple equipment. In this work, natural dyes were used to reduce costs and TiO_2 nanoparticles were synthesized using sol-gel method. Then, DSSC was fabricated based on synthesized TiO_2 and photovoltaic performance was evaluated under AM 1.5 G by measuring current-voltage curves and calculating η , V_{oc} , J_{sc} , and FF .

2. Experimental

2.1. Materials

The Titanium (IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), distilled water, nitric acid (HNO_3), polyethylene glycol ($\text{C}_{10}\text{H}_{18}\text{O}_{10}$), acetonitrile ($\text{C}_2\text{H}_3\text{N}$), potassium iodide (KIO_3) and iodine (I_2), ethylene glycol ($\text{C}_2\text{H}_4\text{O}_2$), platinum (Pt). Syzygium Cumini fruit and fluorine-doped tin oxide (FTO) conductive glass (sheet resistance $10 \Omega/\text{sq}$).

2.2. Preparation of TiO_2 nanoparticles paste

In this method, TiO_2 nanoparticles were synthesized in anatase phase. First, titanium (IV) isopropoxide was added to ethanol under stirring and after few minutes, distilled water was added. Then adding few drops of nitric acid was done to control the pH of prepared solution. To form sol, solution must be stirred vigorously for 30 min, then aging for 24 hrs to obtain gel. For preparing TiO_2 nanoparticles from gel, it must be dried at 120°C then, sintered at 450°C to get white powder [4]. The procedure of TiO_2 synthesis is shown in Fig. 1. Finally, TiO_2 powder and polyethylene glycol were mixed into the mortar until uniform paste was obtained [7].

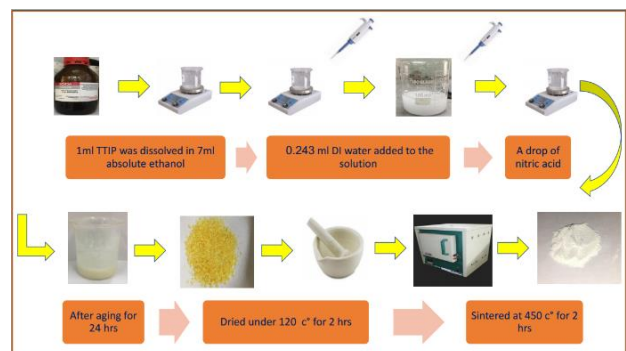


Fig. 1: The schematic of the synthesis route for TiO_2 via sol-gel method

2.3. Preparation of natural dye and electrolyte

It was extracted from fresh Syzygium Cumini fruit and ethanol was used as solvent [8,9]. For preparation of electrolyte solution, first, 10 ml acetonitrile was added to 30 ml ethylene glycol under stirring. Subsequently, 1.375 g potassium iodide and 0.337 g iodine was added

respectively. Prepared electrolyte was stirred until homogenous solution appeared [9].

2.4. Fabrication of DSSC

First, FTO glass substrate ultrasonically cleaned in deionized water, hydrochloric acid, acetone and ethanol respectively and dried at 70 °C. Afterwards, the prepared TiO₂ paste was coated on FTO glass, to make photoanode, by doctor blade method and after a few minutes it was heated at 120 °C then, calcinated at 450 °C. After cooling, the photoanode was immersed in dye solution and kept in darkness for 24 hrs. For the counter electrode, a thin layer of platinum was deposited on another FTO glass substrate. Finally, photoanode and counter electrode were combined together and sealed using surlyn sheet and electrolyte was injected between them. The active area of the electrode was 0.25 cm². The photograph of the fabricated DSSC is given in Fig. 2.

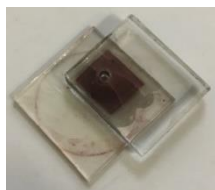


Fig. 2: The fabricated DSSC

3. Results and Discussion

Figure. 3 shows the UV-vis absorption spectra in the range of 300–800 nm, which is shown a peak in 380 nm. The absorption spectra of the prepared TiO₂ nanoparticles become sharper and the absorbance increases. The FT-IR spectroscopy of the sample were studied which were synthesized via sol-gel method in the range of 4000–400 cm⁻¹ and shown in Fig. 4. In this curve, peaks at 425 cm⁻¹ and 932 cm⁻¹ are for O–Ti–O bonding in anatase morphology. The bands centered at 2947 cm⁻¹ and 3312 cm⁻¹ are the characteristic of surface-adsorbed water and hydroxyl groups. Existing fine peaks also relate to the residual components of organic matter and reactions between water and carbon dioxide, while

the last peak is attributed to the TiO₂. As well, XRD pattern was done to determine crystal structure of the prepared TiO₂ powder. The XRD peaks in the range of 2θ from 20°–90°, where the peaks in 20.418°, 37.208°, 38.143°, 48.226°, 54.344°, 55.292°, 63.080°, 70.087°, 75.070°, and 83.114° can be attributed to the 101, 103, 112, 200, 105, 211, 204, 220, 210, and 222 crystalline structures of anatase. This pattern is represented in Fig. 5.

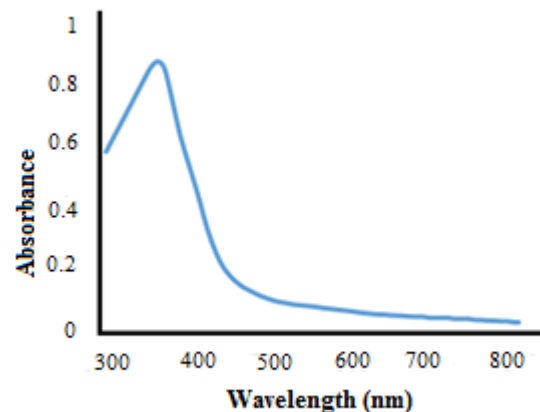


Fig. 3: The UV-visible of the fabricated DSSC

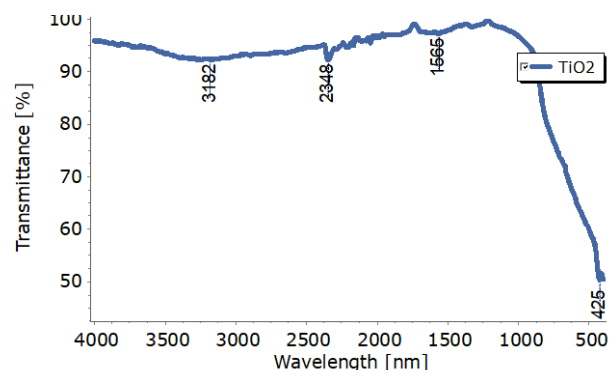


Fig. 4: The FTIR of the fabricated TiO₂ nanoparticles

The current density–voltage (J–V) characteristics is represented in fig. 6 and photovoltaic parameters of fabricated DSSC are calculated from this curve with incident light intensity of 100 mW/cm² and AM 1.5. The efficiency of fabricated cell is 1.36% whereas calculated photovoltaic parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) are 0.88 mA/cm², 0.123 V and 0.376, respectively and with good agreement with pervious works [8,10]. The results approved the existence of free carriers by light

photons absorption. It is expected to enhance the efficiency of dye adsorption by increasing the grain boundaries of the produced TiO₂ using sol-gel method.

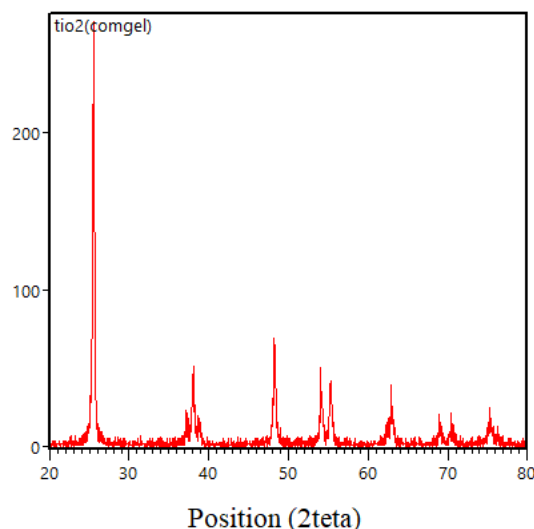


Fig. 5: Powder XRD pattern of the TiO₂ nanoparticles

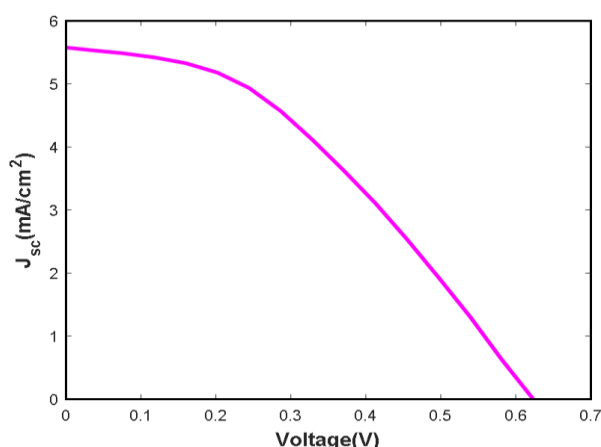


Fig. 6: current density–voltage curve of the fabricated DSSC

4. Conclusion

TiO₂ nanoparticles have been successfully synthesized using sol-gel method. The synthesized TiO₂ nanoparticles were characterized using XRD, and FTIR techniques. The produced nanoparticles were used as a part of photoanode in the DSSCs. The pastes were prepared with simple method and used in the photoanode of the fabricated DSSCs. The crystallography of the pastes, using X-ray illustrated the existence of TiO₂ in the anatase phase in all samples. The fabricated TiO₂-based DSSCs demonstrated a light to the electricity conversion

efficiency of 1.13% with a fill factor of 37.6%, open-circuit voltage of 0.62 V, and short-circuit current of 3.5 mA/cm².

References

- [1] O'Regan, B., & Grätzel, M. (2018). A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films. In *Renewable Energy* (pp. 208-213). □□□□□□□□.
- [2] Sharma, A., Karn, R. K., & Pandiyan, S. K. (2014). Synthesis of TiO₂ nanoparticles by sol-gel method and their characterization. *J Basic Appl Eng Res*, 1(9), 1-5.
- [3] Li, G., Richter, C. P., Milot, R. L., Cai, L., Schmuttenmaer, C. A., Crabtree, R. H., ... & Batista, V. S. (2009). Synergistic effect between anatase and rutile TiO₂ nanoparticles in dye-sensitized solar cells. *Dalton Transactions*, (45), 10078-10080.
- [4] Vijayalakshmi, R., & Rajendran, V. (2012). Synthesis and characterization of nano-TiO₂ via different methods. *Archives of Applied Science Research*, 4(2), 1183-1190.
- [5] Maurya, I. C., Senapati, S., Singh, S., Srivastava, P., Maiti, P., & Bahadur, L. (2018). Effect of Particle Size on the Performance of TiO₂ Based Dye-Sensitized Solar Cells. *ChemistrySelect*, 3(34), 9872-9880.
- [6] Jeng, M. J., Wung, Y. L., Chang, L. B., & Chow, L. (2013). Particle size effects of TiO₂ layers on the solar efficiency of dye-sensitized solar cells. *International Journal of Photoenergy*, 2013.
- [7] Kumar, K. A., Subalakshmi, K., & Senthilselvan, J. (2016). Effect of mixed valence state of titanium on reduced recombination for natural dye-sensitized solar cell applications. *Journal of Solid State Electrochemistry*, 20(7), 1921-1932.
- [8] Golshan, M., Osfour, S., Azin, R., & Jalali, T. (2020). Fabrication of optimized eco-friendly dye-sensitized solar cells by extracting pigments from low-cost native wild plants. *Journal of Photochemistry and Photobiology A: Chemistry*, 388, 112191.
- [9] Gu, P., Yang, D., Zhu, X., Sun, H., Wangyang, P., Li, J., & Tian, H. (2017). Influence of electrolyte proportion on the performance of dye-sensitized solar cells. *AIP Advances*, 9(10), 105219.

[۱۰] Hambali, N. A. M. A., Yusof, N. R., Norhafiz Hashim, M., & Mat Isa, S. S. (۲۰۱۵). Dye-Sensitized Solar Cell Using Syzygium Cumini Fruit as Natural Dye Utilizing Titanium Dioxide. In Applied Mechanics and Materials ۷۵۴-۷۵۵, ۱۱۷۷.