TiO\textsubscript{2} treatment using ultrasonication for bubble cavitation generation and efficiency assessment of a dye-sensitized solar cell

Jae-hun Bae\textsuperscript{a}, Seong-bin Do\textsuperscript{a}, Sung-ho Cho\textsuperscript{a}, Kyung-min Lee\textsuperscript{a}, Sung-Eun Lee\textsuperscript{b,1}, Tae-Oh Kim\textsuperscript{a,b,c,1,*}

\textsuperscript{a} Department of Environmental Engineering, Kumoh National Institute of Technology, Gumi 39253, Republic of Korea
\textsuperscript{b} Department of Applied Biosciences, Kyungpook National University, Daegu 41566, Republic of Korea
\textsuperscript{c} Department of Energy Engineering Convergence, Kumoh National Institute of Technology, Gumi 39177, Republic of Korea

\begin{abstract}
In this study, the impacts of different ultrasonic treatments on TiO\textsubscript{2} particles were determined and they were used to manufacture the photoelectrodes of a dye-sensitized solar cell (DSSC). Two methods were used to prepare TiO\textsubscript{2} particles directly sonicated by an ultrasonic horn, and TiO\textsubscript{2} treated indirectly by an ultrasonic cleaner. TEM, XPS analysis was confirmed that cavitation bubbles generated during ultrasonication resulted in defects on the surface of TiO\textsubscript{2} particles, and the defect induced surface activation. To understand the effect of TiO\textsubscript{2} surface activation on energy conversion efficiency of DSSC, ultrasonic horn DSSC and ultrasonic cleaner DSSC were prepared. The UV–vis analysis exhibited that the ultrasonic horn DSSC possessed higher dye adsorption when compared to the ultrasonic cleaner DSSC, and the EIS analysis confirmed that the electron mobility was greatly increased in the ultrasonic horn DSSC. The energy conversion efficiency of the ultrasonic horn DSSC was measured to be 3.35%, which is about 45% increase in comparison to that of the non-ultrasonic treated DSSC (2.35%). In addition to this regard, recombination resistance of ultrasonic horn DSSC was calculated to be 450 $\Omega \cdot \text{cm}^2$, increasing more than two times compared to the non-ultrasonic treated DSSC (200 $\Omega \cdot \text{cm}^2$). Taken together, these ultrasonic treatments significantly improved the energy conversion efficiency of DSSC, which was not tried in DSSC-related research, and might lead us to develop more efficient practical route in the manufacturing of DSSC.
\end{abstract}

1. Introduction

Solar cells are clean and renewable energy sources that do not cause environmental pollution. Depending on their constituent chemicals, solar cells are divided into silicon solar cells [1,2], thin film solar cells [3,4,5], organic solar cell [6,7], dye-sensitized solar cells (DSSCs) [8,9], and perovskite solar cells [10,11]. Among them, silicon solar cells are the most commonly used because they show a high efficiency of 25% or more [1]. However, they are expensive because of their complicated manufacturing process and high energy consumption [2]. To compensate for these disadvantages, many researchers have developed new solar cells to replace silicon solar cells, and one of them is the DSSC. The DSSC was first introduced by Grätzel in 1991. It generates electricity by irradiating light energy to a dye adsorbed on a semiconductor photoanode, and the excited electrons trigger a redox reaction in the electrolyte [12]. TiO\textsubscript{2}, which is a metal oxide semiconductor, is economical and has high physical and thermal stabilities, making it the most suitable photoanode for DSSCs [8,12]. Although the DSSC using TiO\textsubscript{2} has low cost and high stability, it has low dye adsorption and high electron recombination rates, which pose as obstacles to the efficiency improvement [9].

One of the methods of increasing the TiO\textsubscript{2} photoelectrode efficiency is doping with a transition metal, such as Cu [13], Zn [14], Zr, and W [15]. In our previous studies, doping with various transition metals also improved the TiO\textsubscript{2} efficiency. Park et al. extended the reactive region of the photoelectrode to the visible region by Cu doping and achieved a high efficiency of up to 11.35% [16]. Meanwhile, Kim et al. improved the dye adsorption by the post-treatment of Zr oxide in TiO\textsubscript{2} and obtained an efficiency of approximately 7.03% [17]. Lee et al. improved the specific surface area and dye adsorption by doping TiO\textsubscript{2} with SiO\textsubscript{2}.

\begin{footnotesize}
\begin{itemize}
  \item \textsuperscript{a} Corresponding author at: Department of Environmental Engineering, Kumoh National Institute of Technology, Gumi 39253, Republic of Korea.
  \item \textsuperscript{1} The authors equally contributed to the paper as corresponding author.
  \item \textsuperscript{*} E-mail address: tokim@kumoh.ac.kr (T.-O. Kim).
\end{itemize}
\end{footnotesize}

https://doi.org/10.1016/j.ultsonch.2022.105933
Received 9 November 2021; Received in revised form 20 January 2022; Accepted 23 January 2022
Available online 29 January 2022
1350-4177/© 2022 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
and N. They enhanced the energy conversion efficiency by up to 8.68% [45]. On the contrary, current studies have encountered difficulties when adding complex heat treatment processes, such as the hydrothermal method, for doping transition metal, which consumes much time to manufacture. Therefore, a new process for improving the TiO$_2$ efficiency must be developed.

The methods of preparing TiO$_2$ into a photoanode are spin coating [18], dip coating [19], screen printing [20], and doctor blade method [20], among others. Spin coating can smoothly control the voids and thickness of the photoelectrode, but the paste may aggregate at the edges due to a centrifugal force [21]. In dip coating, the photoelectrode thickness is uniform and thin; however, as a limitation, the surface is formed non-uniformly when the paste concentration is high [22]. The screen-printing technology is advantageous for the large-scale production of paste due to uniform thickness. However, in this method, paste is thickly applied, consequently impairing the DSSC efficiency [20]. The doctor blade method is a general photoanode manufacturing method, in which TiO$_2$ particles are uniformly distributed inside the paste, and particle loss is small; however, when high-concentration paste is applied, the thickness is not constant, thereby needing improvement [20].

In this study, we will try to improve the energy conversion efficiency of the DSSC by adding a simple and new “sonicated” process to the currently used doctor blade preparation method. Sonication is one of the processes used to form nanoparticles. It leads to surface activation by forming defects on the particle surface as a cavitation reaction [23,24,25]. The cavitation reaction is defined as a process in which bubbles in a fluid are formed, grown, and collapsed [26,27]. It was confirmed that the cavitation reaction is a physical and chemical reaction that oxidizes and activates the catalyst surface [28,29,30]. Hafeez et al. reported that the high heat and pressure accompanying the cavitation reaction cause defects and deformation on the particle surface, which contribute to the catalyst activation [23]. Narakaew attempted to improve the activation and reactivity of the TiO$_2$ surface by the cavitation phenomenon [36]. In addition, Stucchi et al. improved the dispersion of the active area by dispersing the particles through ultrasonication [35,36]. Thus, ultrasonic treatment could result in surface activation and improves the performance of catalysts and photocatalysts by uniformly dispersing materials. However, the sonication process has rarely been applied in the DSSC studies reported so far. Therefore, in the present study, a DSSC was manufactured by applying ultrasonicated TiO$_2$ to the photoelectrode. Its applicability and superiority are then investigated. The effect of TiO$_2$ treated with ultrasonic cleaner and ultrasonic horn on the DSSC efficiency is also studied.

**Fig. 1.** (a-c) SEM images of (a) TiO$_2$; (b) ultrasonic cleaner-TiO$_2$; (c) ultrasonic horn-TiO$_2$. And (d-f) TEM images of (d) TiO$_2$; (e) ultrasonic cleaner-TiO$_2$; (f) ultrasonic horn-TiO$_2$. 
2. Experimental

2.1. Materials

The DSSC used in this experiment was prepared using TiO$_2$ (anatase 99.9%, US Research Nanomaterials, Houston, TX), α-terpineol (98.5%, Samchun Chemicals, Seoul, South Korea), chloroplatinic acid hydrate (Sigma Aldrich, St. Louis, MO), N719 dye (Solaronix, Aubonne, Swiss), ethanol (HPLC grade, Duksan Co., Ansan, South Korea), and ethyl cellulose 10 cP (extra pure, Daejung Chemicals & Metals, Siheung, South Korea). An ultrasonic cleaner (JAC2010, KODO Technical Research Co., Hwasung-si, South Korea) and an ultrasonic horn (VC750, Sonics & Materials, Newtown, CT) were used as the ultrasonic treatment equipment.

2.1.1. Preparation of the TiO$_2$ (commercial TiO$_2$) paste

The TiO$_2$ paste was prepared through the sol–gel method with 25 ml ethanol, 2.15 ml α-terpinol, and 0.6 ml distilled water added to 2 g of TiO$_2$ and stirred at 120 °C at 300 rpm for 15 min. Subsequently, 0.3 g of ethyl cellulose was added and stirred until the paste was completed. The complete paste was applied to the FTO plate by the doctor blade method, which is a method of coating with a constant thickness using a blade, and the process is as follows. In order to prepare a photoelectrode having an area of 5 mm $\times$ 5 mm on FTO glass, the other areas were masked. After this process, a certain amount of paste was repeatedly coated on glasses with 5 to 10 times using a blade, and the TiO$_2$ photoelectrode was manufactured by a calcination process at 450 °C for 2 h at a temperature increase rate of 5 °C/min. The photoelectrodes were immersed in an N719 dye (0.5 mM) in ethanol at room temperature for 24 h.

2.1.2. Preparation of the ultrasonic cleaner-TiO$_2$ paste

The ultrasonic cleaner-TiO$_2$ paste manufacturing added an indirect ultrasonic treatment process to the same method for the TiO$_2$ paste preparation. After adding 2 g of TiO$_2$ to 50 ml of ethanol, ultrasonic treatment (intensity high) was indirectly performed in an ultrasonic cleaner bath for 30 min to prepare an ultrasonic cleaner-TiO$_2$ solution. α-Terpinol (2.15 ml) and 0.6 ml distilled water were added to the ultrasonic cleaner-TiO$_2$ solution and stirred at 120 °C at 300 rpm for 15 min. After this process, 0.3 g ethyl cellulose was added and stirred until the paste was completed. An ultrasonic cleaner-TiO$_2$ photoelectrode was then manufactured in the same manner as that of TiO$_2$.

2.1.3. Manufacture of the ultrasonic horn-TiO$_2$ paste

The ultrasonic horn-TiO$_2$ paste was manufactured in the same manner as the ultrasonic cleaner-TiO$_2$ paste. Ultrasonic treatment was directly performed. An ultrasonic horn-TiO$_2$ solution was prepared by directly sonicating a solution, in which 2 g of TiO$_2$ was added to 50 ml of ethanol with an ultrasonic horn for 30 min. Thereafter, an ultrasonic horn-TiO$_2$ photoelectrode was manufactured in the same manner as the ultrasonic cleaner-TiO$_2$.

2.1.4. Counter electrode manufacturing and joining

The counter electrode was ultrasonically cleaned in ethanol for 15 min after drilling two holes through which the electrolytes could be injected in the FTO glass. A H$_2$PtCl$_6$ solution was coated on the washed FTO glass by spin coating and then calcined at 350 °C for 1 h to prepare a counter electrode. After joining the prepared counter electrode and the photoanode, Iodolyte AN-50 was injected as an electrolyte, and the hole was closed to complete the DSSC.

2.2. Characterisation

The scanning electron microscopy (SEM, ×3000), transmission electron microscopy (TEM, ×250000), Brunauer–Emmett–Teller (BET), and X-ray diffraction (XRD, scan rate 5°/min), and X-ray photoelectron spectroscopy (XPS) analyses were performed in powder form. XRD and XPS were performed to understand the shape and structure of the manufactured TiO$_2$. The specific surface area was measured through BET. The surface properties were analyzed through SEM and TEM analyses. The prepared DSSC was analyzed with photo-electrochemical
data using 2400 source (Keithley Instruments) under AM 1.5 illumination (100 mW/cm²). The electron mobility of the electrode was analyzed by EIS. The chemical capacitance and the recombination resistance were calculated using the EIS and efficiency data.

3. Results and discussion

3.1. Characteristics analysis of TiO₂

The SEM analysis was performed to determine the dispersion of TiO₂, ultrasonic cleaner-TiO₂, and ultrasonic horn-TiO₂ (Fig. 1). The particles in TiO₂ (Fig. 1 a) were agglomerated, whereas those in the ultrasonically treated ultrasonic cleaner-TiO₂ and ultrasonic horn-TiO₂ were dispersed (Fig. 1 b and c). The dispersion degree of the directly applied ultrasonic horn-TiO₂ was relatively higher than that of the indirectly applied ultrasonic cleaner-TiO₂, which was consistent with the results of the previous studies showing that ultrasonic waves affect the particle dispersion [36]. The BET analysis was performed to determine the change in the specific surface area before and after the sonication of each TiO₂ (Table 1). The specific surface areas were measured to be approximately 87.50 m²/g for TiO₂, approximately 88.15 m²/g for ultrasonic cleaner-TiO₂, and approximately 87.44 m²/g for ultrasonic horn-TiO₂. Although the ultrasonic waves affected the particle dispersion, they were thought to not contribute to the changes in the specific surface area.

The previous analysis showed the external change of the TiO₂ particles by ultrasonication. The changes in the properties of the inside of the particles were confirmed by the results of the TEM, XRD, and XPS analyses. Fig. 1 (e–h) depict the TEM images of each sample measured at 250,000 × magnification. Accordingly, TiO₂ particles with a diameter ranging from 30 nm to 50 nm were observed. The roughness of the outside of the particle was increased by the ultrasonication, which is more clearly shown in the insets describing TiO₂ (Fig. 1 e) and ultrasonic horn-TiO₂ (Fig. 1 f). It was assumed that the ultrasonic wave was applied to the liquid medium (ethanol) mixed with TiO₂, and the generated cavitation bubble formed a defect on the particle surface. The TiO₂ surface defects occurred in the form of an oxygen vacancy or Ti⁴⁺ [31,32] and did not significantly affect the surface area of the particle.

Fig. 3. (a) XPS survey spectrum Ti 2p of TiO₂, ultrasonic cleaner-TiO₂, ultrasonic horn-TiO₂; (b) XPS survey spectrum O 1s of TiO₂, ultrasonic cleaner-TiO₂, ultrasonic horn-TiO₂.
Itself. It may, however, contribute to the particle surface activation [33]. This is related to the XPS analysis results, which will be described later. The TiO$_2$ surface activation caused by the defects improved the photocatalytic performance [34].

Fig. 2 shows the XRD analysis results comparing the ultrasonic cleaner/ultrasonic horn-TiO$_2$ and TiO$_2$. Three spectra with almost identical diffraction peaks were identified, regardless of ultrasonication. The distinct diffraction peaks at 25°, 38°, 48°, 54°, and 55° were consistent with the intrinsic spectrum of the anatase phase TiO$_2$ (JCPDS no.: 88–1175 and 84–1286) [37,38]. This indicates that no change occurred in the crystal compositions of the three TiO$_2$ used herein.

The XPS analysis was performed to analyze the oxidation state of each TiO$_2$ surface. Fig. 3 depicts the obtained results. All XPS analyses were corrected for C 1 s (284.6 eV). In the Ti 2p spectrum, two peaks corresponding to Ti$^{4+}$ (i.e., Ti$^{4+}$ 2p$_{1/2}$ and Ti$^{4+}$ 2p$_{3/2}$) and one peak representing Ti$^{3+}$ (i.e., Ti$^{3+}$ 2p$_{1/2}$) were analyzed. The Ti$^{3+}$ 2p$_{1/2}$ peak originated from the oxygen vacancy on the TiO$_2$ surface caused by ultrasonication, indicating that the ultrasonic wave activated the TiO$_2$ surface [39,40]. The proportion of Ti$^{3+}$ on each TiO$_2$ surface was the highest in the ultrasonic horn-TiO$_2$ (8.38%). Those of the ultrasonic cleaner-TiO$_2$ and TiO$_2$ were 6.76% and 5.22%, respectively. These results demonstrate that ultrasonic treatment induced the TiO$_2$ surface activation.

The O 1 s spectrum showed the oxygen species present on the TiO$_2$ surface. The peaks corresponding to the lattice oxygen (bridging O, 529–530 eV) and active oxygen (central O, 530–532 eV) of TiO$_2$ were found in the O 1 s spectrum [41–43]. As shown in Fig. 3, the active oxygen in the ultrasonic horn-TiO$_2$ was 33.96%; that in the ultrasonic cleaner-TiO$_2$ was 31.27%; and that in C-TiO$_2$ was 27.89%. These results were consistent with those of the Ti 2p spectrum, in which the ultrasonic treatment improved the active oxygen content of TiO$_2$ and activated the TiO$_2$ surface.

Fig. 4. UV-visible absorption spectrum for the dye adsorption assessment. (a) TiO$_2$; (b) ultrasonic cleaner-TiO$_2$; (c) ultrasonic horn-TiO$_2$.

Fig. 5. EIS Nyquist plot (under dark condition) of (a) TiO$_2$; (b) ultrasonic cleaner-TiO$_2$; (c) ultrasonic horn-TiO$_2$.
3.2. Characteristics analysis of DSSC

The previous analysis results confirmed that ultrasonic treatment activates the TiO$_2$ surface. UV–vis, EIS, J-V graph analyses were employed to prove how the surface activation of TiO$_2$ affected the DSSC efficiency. First, the ultraviolet–visible (UV–vis) spectrum was used to check the dye adsorption, which was the main electron source of the DSSC herein, to confirm the increase in the dye adsorption (Fig. 4). To evaluate the amount of dye adsorption, the absorbance was measured by adsorbing dye to the photoelectrode for 24 h, then desorbing it with 1 mM KOH solution [44]. At 500 nm wavelength, the absorbance of the ultrasonic horn was significantly higher than that of the other two samples. The amount of dye adsorbed on the photoelectrode surface was observed in the following order: ultrasonic horn-TiO$_2$ > ultrasonic cleaner-TiO$_2$ > TiO$_2$.

When compared to other two treatments, the ultrasonic horn-TiO$_2$ exhibited a higher dye adsorption caused by the particle surface activation, which was due to the cavitation bubbles with particle dispersion [45]. The high dye adsorption of the ultrasonic cleaner-TiO$_2$ and the ultrasonic horn-TiO$_2$ acted as a key factor for improving the energy conversion efficiency of the DSSC by increasing the current density.

### Table 2
Summary of energy conversion efficiency of the DSSCs according to sonication.

| Samples                | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | $\eta$ (%) |
|------------------------|----------------------|--------------|--------|-------------|
| TiO$_2$                | 5.54                 | 0.68         | 45.8   | 2.35        |
| Ultrasonic cleaner-TiO$_2$ | 6.40                 | 0.68         | 64.5   | 2.82        |
| Ultrasonic horn-TiO$_2$ | 7.47                 | 0.72         | 62.3   | 3.35        |

### Table 3
Parameters for calculating the chemical capacitance and the recombination resistance. $\Delta E_c$ means the difference in conduction band energy ($E_c$) between each material. Since these samples have the same chemical composition, there is no change in the $E_c$ value.

| Samples                | $\Delta E_c$       | $J_0$ (mA/cm$^2$) | $R_0$ ($\Omega$ cm$^2$) | $R_s$ (k$\Omega$) |
|------------------------|--------------------|-------------------|-------------------------|------------------|
| TiO$_2$                | Ref. $5.54 \times 10^{-3}$ | $3.81 \times 10^6$ | 43.46                   |
| Ultrasonic cleaner-TiO$_2$ | 0                  | $6.40 \times 10^{-3}$ | $4.54 \times 10^6$ | 26.88 |
| Ultrasonic horn-TiO$_2$ | 0                  | $7.50 \times 10^{-3}$ | $8.30 \times 10^6$ | 25.12 |

**Fig. 6.** Photocurrent density–voltage (J-V) graph of the DSSCs (under one-sun illumination of 1000 mW/cm$^2$). (a) TiO$_2$; (b) ultrasonic cleaner-TiO$_2$; (c) ultrasonic horn-TiO$_2$.

**Fig. 7.** Graphs for the (a) chemical capacitance and the (b) recombination resistance of TiO$_2$, ultrasonic cleaner-TiO$_2$, ultrasonic horn-TiO$_2$. 

3.2. Characteristics analysis of DSSC

The previous analysis results confirmed that ultrasonic treatment activates the TiO$_2$ surface. UV–vis, EIS, J-V graph analyses were employed to prove how the surface activation of TiO$_2$ affected the DSSC efficiency. First, the ultraviolet–visible (UV–vis) spectrum was used to check the dye adsorption, which was the main electron source of the DSSC herein, to confirm the increase in the dye adsorption (Fig. 4). To evaluate the amount of dye adsorption, the absorbance was measured by adsorbing dye to the photoelectrode for 24 h, then desorbing it with 1 mM KOH solution [44]. At 500 nm wavelength, the absorbance of the ultrasonic horn was significantly higher than that of the other two samples. The amount of dye adsorbed on the photoelectrode surface was observed in the following order: ultrasonic horn-TiO$_2$ > ultrasonic cleaner-TiO$_2$ > TiO$_2$.

When compared to other two treatments, the ultrasonic horn-TiO$_2$ exhibited a higher dye adsorption caused by the particle surface activation, which was due to the cavitation bubbles with particle dispersion [45]. The high dye adsorption of the ultrasonic cleaner-TiO$_2$ and the ultrasonic horn-TiO$_2$ acted as a key factor for improving the energy conversion efficiency of the DSSC by increasing the current density.
Through the EIS analysis, impedance was measured to determine the electron transfer resistance. Fig. 5 depicts the EIS data observed under dark conditions. The semicircle in Fig. 5 depicts the charge transfer resistance measured at approximately 15 kΩ with TiO₂ being the highest. The semicircle size of the ultrasonic cleaner-TiO₂ and the ultrasonic horn-TiO₂ was approximately 7–8 kΩ, confirming that the charge transfer resistance was 50% lower than that of TiO₂. The resistance received by the electrons was low when the charge transfer resistance was low; thus, the current flowed well and may act as a factor for improving the DSSC efficiency.

The energy conversion efficiency of each TiO₂ photoanode was evaluated. Fig. 6 shows the J–V graph measuring the energy conversion efficiency. Table 2 lists the parameters. The energy conversion efficiency of the ultrasonic cleaner-TiO₂ was 2.82%, which improved by approximately 20% compared to TiO₂ (2.35%). The ultrasonic horn-TiO₂ showed an efficiency of 3.35%, which was 43% higher than that of TiO₂ (2.35%) and approximately 19% higher than that of the ultrasonic cleaner-TiO₂. The amount of dye adsorption was increased by the dispersion effect of ultrasonication and the activation effect of the TiO₂ surface, which increased the current density. In conclusion, sonication contributed to the increase of the DSSC efficiency by lowering the electron transfer resistance and increasing the current density.

The chemical capacitance (C₋) and the recombination resistance (R₋) were calculated to confirm the electrical characteristics of the DSSCs prepared using TiO₂ as a photoelectrode. The two calculations were based on the method proposed by Bisquert and the results of our previous study [44,48,49,50]. Table 3 shows the parameters required for the calculation. In the table, ΔE denotes the difference in E between each TiO₂. We found no change in the E value because the materials were chemically identical to each other. The R₋ value is a parameter that determines the effect on the recombination process (Eq. (4)). The R₋ value indicates the series resistance of the DSSC and obtained herein using the EIS data.

\[ C₋ = \frac{L}{(1 - p)/q\varepsilon(E_{F0})} \]  

(1)

In Eq. (1), L denotes the TiO₂ film thickness; p denotes the photo-electrode porosity; and q denotes the elementary charge.

\[ g(E_{F0}) = \frac{a_{N_i}}{k_B T} \exp \left( \frac{\varepsilon(E_{F0} - E_C)}{k_B T} \right) \]  

(2)

Eq. (2) presents the Fermi level (E₀), Boltzmann constant (k₀), total density of the bandgap states (N₀), and the exponent of the electrons below the conduction band. It is calculated using the constant (a) for the parameter for the exponential trap distribution of electrons under the conduction band.

\[ R₋ = R_0 \exp \left[ -\frac{qV_{F0}}{k_B T} \right] \]  

(3)

The recombination resistance (R₋) is calculated using Eq. (3). The variable V₀ (Fermi level voltage) important for the R₋ calculation is calculated using Eq. (5). Vappl represents the applied voltage.

\[ R_0 = \frac{k_B T}{q \mu F_{appr}} \exp \left( \frac{qV_{appr}}{k_B T} \right) \]  

(4)

\[ V_{appr} = V_F - jR_c \]  

(5)

\[ V_{ch} = V_F - \Delta E_{frac}/q \]  

(6)

The equivalent common conduction band voltage (Vcb) of the V₀ value had the same value as the V₀ because the material used for each TiO₂ photoanode is chemically the same. Therefore, the chemical capacitance and the recombination resistance data using Vcb were not presented herein.

The chemical capacitance in Fig. 7(a) showed similar C₋ values because each DSSC applied to the calculation is chemically the same material. Meanwhile, the recombination resistance in Fig. 7(b) illustrated values of approximately 200 Ω cm² for TiO₂ and approximately 450 Ω cm² for ultrasonic horn-TiO₂ at V₀ 0.5 V. The R₋ values increased more than twice because the open-circuit voltage was increased by the effect of the ultrasonic treatment. The increase in the recombination resistance was one of the factors that increased the energy conversion efficiency along with the increases of the dye adsorption and the current density.

4. Conclusions

In this study, a TiO₂ photoelectrode was fabricated through a simple ultrasonication treatment. The surface area change of TiO₂ was analyzed by performing SEM and TEM analyses. Ultrasonic treatment greatly improved the particle dispersion and activated the TiO₂ surface. The XRD analysis confirmed that the anatase structure was maintained, even after ultrasonic treatment. The structural TiO₂ surface activation was analyzed by XPS, and the results showed that the cavitation bubble increased the active area of TiO₂. The effect of the TiO₂ surface activation on the DSSC efficiency was investigated through UV–vis and EIS analyses. The UV–vis analysis revealed that sonication significantly increased the dye adsorption. Meanwhile, the EIS analysis confirmed that sonication reduced the charge transfer resistance. Although the chemical capacitance of each TiO₂ was calculated, the materials used in each DSSC were chemically identical, showing similar capacities. The measurement of the energy conversion efficiency of the DSSC depicted that the DSSC consisting of ultrasonic horn-TiO₂ had an energy conversion efficiency of 3.35%, displaying approximately 45% of improvement compared to TiO₂ (2.35%). In addition, the recombination resistance was calculated using the open-circuit voltage and current density values of the DSSC. The results confirmed that ultrasonic treatment contributed to efficiency improvement by increasing the recombination resistance. In conclusion, the simple and effective sonication described in this paper will be very helpful in improving the DSSC efficiency.

Declaration of Competing Interest

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

Acknowledgements

This research was supported by Kumoh National Institute of Technology (202001120001).

References

[1] M.A. Green, The path to 25% silicon solar cell efficiency: History of silicon cell evolution, Prog. Photovoltaics Res. Appl. 17 (3) (2009) 183–189, https://doi.org/10.1002/pip.v17.10002/pip.892.
[2] T.M. Razykov, C.S. Ferekides, D. Morel, E. Stefanakos, H.S. Ullal, H.M. Upadhya, Solar photovoltaic electricity: Current status and future prospects, Sol. Energy 85 (8) (2011) 1580–1608, https://doi.org/10.1016/j.solener.2010.12.002.
[3] W. Li, R. Yang, D. Wang, C²Fe solar cell performance under high-intensity light irradiance, Sol. Energy Mater. Sol. Cells 123 (2014) 249–254, https://doi.org/10.1016/j.solmat.2014.01.021.
[4] A. Chirila, S. Buecheler, F. Pianezzi, P. Bloesch, C. Greteener, A.R. Uhl, C. Fella, L. Kranz, J. Perrenoud, S. Seyfiling, R. Verma, N. Sishikawa, V.E. Romanyuk, G. Bilger, A.N. Tiwari, Highly efficient Ca (In, Ga) Se 2 solar cells grown on flexible polymer films, Nat. Mater. 10 (11) (2011) 857–861, https://doi.org/10.1038/nmat3122.
[5] S.M. Hubbard, C.D. Cress, C.G. Bailey, R.P. Raffaelli, S.G. Bailey, D.M. Wilt, Effect of strain compensation on quantum dot enhanced GaAs solar cells, Appl. Phys. Lett. 92 (12) (2008) 123512, https://doi.org/10.1063/1.2903699.
[6] M.E. Ragoussi, T. Torres, New generation solar cells: concepts, trends and perspectives, Chem. Commun. 51 (19) (2015) 3957–3972, https://doi.org/10.1039/C4CC09888A.
[7] T.R. Andersen, H.F. Dam, M. Hösel, M. Helgesen, J.E. Carle, T.T. Larsen-Olsen, S. A. Gevorgyan, J.W. Andreasen, J. Adams, N. Li, F. Machui, G.D. Spyropoulos.
[28] D. Panda, S. Manickam, Cavitation technology—The future of greener extraction method: A review on the extraction of natural products and process intensification mechanism and perspectives, Applied Sciences 9 (4) (2019) 766, https://doi.org/10.3390/app9040766.

[29] P.I. Gousma, M.J. Mills, Anatase-to-rutile transformation in titania powders, J. Am. Ceram. Soc. 84 (3) (2001) 619–622, https://doi.org/10.1111/j.1151-2916.2001.01149.x.

[30] D.G. Shchukin, E. Skorb, V. Belova, H. Mohwald, Ultrasonic cavitation at solid surfaces, Adv. Mater. 23 (17) (2011) 1922–1934.

[31] X. Chen, L. Liu, Y.P. Peter, S.S. Mao, Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals, Science 331 (6018) (2011) 746–750, https://doi.org/10.1126/science.1200448.

[32] X. Pan, M.Q. Yang, X. Fu, N. Zhang, Y.J. Xu, Defective TiO2 with oxygen vacancies: Synthesis, properties and photocatalytic applications, Nanoscale 5 (9) (2013) 3601–3614, https://doi.org/10.1039/c3nr00476g.

[33] S. Naraoke, The nano-TiO2 synthesis using ultrasonic assisted sol-gel method and its photocatalytic degradation of methylene blue, J. Ceram. Process. Res. 18 (1) (2017) 36–40.

[34] T. Xia, Y. Zhang, J. Munowich, X. Chen, Vacuum-treated titanium dioxide nanocrystals: Optical properties, surface disorder, oxygen vacancy, and photocatalytic activities, Catal. Today 225 (2014) 2–9, https://doi.org/10.1016/j.cattod.2013.08.026.

[35] M. Stauch, C.L. Bianchi, C. Agrivisius, V. Piferi, B. Neppolian, G. C. Boftito, Ultrasonic assisted synthesis of Ag-decorated TiO2 active in visible light, Ultrason. Sonochem. 40 (2018) 282–288, https://doi.org/10.1016/j.ultsonch.2017.07.016.

[36] A. Katamipour, M. Farzam, I. Danaye, Effects of sonication on anticrocorrosive and mechanical properties of electrophoresited Ni–Zn-TiO2 nanocomposite coatings, Surf. Coat. Technol. 254 (2014) 358–363, https://doi.org/10.1016/j.surfcoat.2014.06.043.

[37] K. Thamapb, P. Limwunaw, B. Ngotawornchai, Phase characterization of Ti2O2 powder by XRD and TEM, Agric. Nat. Resour. 42 (5) (2008) 357–361.

[38] R. Yoshida, Y. Suzuki, Y. Yoshikawa, Syntheses of TiO2 (B) nanowires and TiO2 anatase nanowires by hydrothermal and post heat treatments, J. Solid State Chem. 178 (5) (2007) 2179–2185, https://doi.org/10.1016/j.jssc.2005.04.025.

[39] M. Dhayal, J. Jun, H.B. Gu, K.H. Park, Surface chemistry and optical property of TiO2 thin films treated by low-pressure plasma, J. Solid State Chem. 180 (10) (2007) 2666–2701, https://doi.org/10.1016/j.jssc.2007.06.037.

[40] K. Safeen, V. Micheli, R. Bartalli, G. Gaiteri, A. Safeen, H. Ullah, N. Laidani, Synthesis of conductive and transparent Nb-doped TiO2 films: role of the target material and sputtering gas composition, Mater. Sci. Semicond. Process. 66 (2017) 74–80, https://doi.org/10.1016/j.mssp.2017.04.012.

[41] M.Z. Atashbar, H.H. Sun, B. Gong, W. Wlodarski, L. Lamb, XPS study of Nb-doped oxygen sensing TiO2 thin films prepared by sol-gel method, Thin Solid Films 326 (1–2) (1998) 238–244, https://doi.org/10.1016/S0040-6090(98)00534-3.

[42] R. Walewski, J. Domaradzki, D. Wojcechowska, D. Kaczmarek, A. Borkowska, E. L. Procio, A. Cisewski, Surface characterization of TiO2 thin films obtained by high-energy reactive magnetron sputtering, Appl. Surf. Sci. 254 (14) (2008) 4936–4940, https://doi.org/10.1016/j.apsusc.2007.12.017.

[43] H. Perron, J. Vandenborne, C. Domain, R. Drot, J. Roques, E. Simoni, J.-J. Ehrhardt, K. Pathy, A. Penisson, M. Capdevila, Combined investigation of water sorption on TiO2 rutile (1 1 0) single crystal face: XPS vs. periodic DFT, Surf. Sci. 601 (2007) 518–527, https://doi.org/10.1016/j.susc.2006.10.006.

[44] S.B. Kim, J.Y. Park, C.S. Kim, K. Okuyama, S.E. Lee, H.D. Jang, T.O. Kim, Effects of graphene in dye-sensitized solar cells based on nitrogen-doped TiO2 composite, J. Phys. Chem. C 119 (29) (2015) 16552–16559, https://doi.org/10.1021/jp510239f.

[45] R. Mølø, J. Tøtta, K. Sakai, Y. Niida, Y. Koshiba, L. Le, K. Nakamore, Y. Ueda, Organic solvent based TiO2 dispersion paste for dye-sensitized solar cells prepared by industrial production level procedure, J. Mater. Sci. 46 (5) (2011) 1341–1350, https://doi.org/10.1007/s10853-010-4925-2.

[46] M. Dholke, K. Sahu, V.V.S. Murty, Cu-doped TiO2 nanoparticles/graphene composites for efficient dye-sensitized solar cells, Sol. Energy 220 (2021) 418–424, https://doi.org/10.1016/j.solener.2021.03.072.

[47] K. Sahai, M. Dhome, V.V.S. Murty, Microwave-assisted hydrothermal synthesis of Cu-doped TiO2 nanoparticles for efficient dye-sensitized solar cell with improved open-circuit voltage, Int. J. Energy Res. 45 (4) (2021) 5423–5432, https://doi.org/10.1002/er.16169.

[48] M.L. Lee, J.Y. Park, C.S. Kim, K. Okuyama, S.E. Lee, T.O. Kim, Improvement of light scattering capacity in dye-sensitized solar cells by doping with SiO2 nanoparticles, J. Power Sources 327 (2016) 96–103, https://doi.org/10.1016/j.jpowsour.2016.07.032.

[49] J. Bisquert, Chemical capacitance of nanostructured semiconductors: its origin and significance for nanostructured solar cells, PCCP 25 (4) (2023) 5360–5364, https://doi.org/10.1039/d3cp01909a.

[50] F. Fabregat-Santiago, G. García-Belmonte, I. Moro-Serna, J. Bisquert, Characterization of nanostructured hybrid and organic solar cells by impedance spectroscopy, PCCP 13 (20) (2011) 9083–9118, https://doi.org/10.1039/C9CP02249G.